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PREFACE.

THE Council desires to express its indebtedness to Mr. E. V. Evans, who suggested the issue of these Reports of the Progress of Applied Chemistry, and to his colleagues of the Publication Committee. The manuscript of the published sections was received by the date arranged, but as the compilers of the sections on fibres, dyeing, metallurgy, electrochemistry, and sugar were unable to send in their copy in time, it was decided to present an incomplete volume rather than delay publication any further.

It will be observed that, apart from the sections mentioned above, some of the sections of the classification followed in the Society's Journal are not covered in these Reports. The sections on Agricultural Chemistry, the Chemistry of Foods, and Analysis are dealt with in the admirable series of Annual Reports issued by the Chemical Society, whilst for obvious reasons it is undesirable to include a section on Explosives at the present time.

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REPORTS

OF THE

PROGRESS OF APPLIED CHEMISTRY.

FUEL AND HEATING.

By J. W. Cobb, B.Sc.,

Livesey Professor of Fuel and Gas Industries, Leeds University.

In the period under review much experimental work in Europe has been suspended and many activities have been secret, bringing into prominence the published work of American investigators, and marking the development of public scientific services in the United States.

Chemistry of Coal.

Jones and Wheeler[1] have continued their examination of coal by the method of vacuum distillation, with examination of the liquid products. The portions of a Durham coal as separated by solvents were distilled. By a first treatment with pyridine, the "resinous" portion was extracted and the "humus" substances (*a*) separated. The resinous portion was extracted with chloroform, leaving a residue (*b*), the soluble portion (*c*) being recovered by evaporation. (*a*) and (*b*) were considered to be mainly "humus," and the resinous substances only to have been decomposed. (*a*) and (*b*) yielded only small quantities of liquid on distillation up to 400° C., mainly phenols; (*c*) yielded 40–50 % of liquid, mainly paraffins, olefines, and naphthenes, but no phenols. The authors suggest that the presence of the furan grouping is responsible for the production of phenol, this grouping being present in the humus substances, which are regarded as derived from the original woody fibre or cellulose of the coal plants. The presence of the furan group in cellulose is known, as also that in distillation it breaks down with the production of phenol. The results of this paper are to be taken and valued in conjunction with others previously obtained by the thorough work of Dr. Wheeler and his collaborators.

[1] *J. Chem. Soc.*, 1915, **107**, 1318; *J.*, 1915, 1043.

Parr and Hadley[2] have also made experiments on the separation of the constituents of coal by the use of solvents. Pyridine has been used most commonly hitherto, but is not altogether satisfactory, as there is undoubtedly retention of solvent by the fractions obtained. It is therefore not possible to examine the distribution of the nitrogen in the residue and extract. These authors believe that phenol behaves towards coal as a true solvent, and is chemically inert to the constituents. They used phenol in the examination of a number of American coals, their method being to extract 5 grammes of coal with phenol at 110° C. for twenty hours.

The conditions governing the formation of ammonia and cyanogen in the carbonization of coal have been examined by Simmersbach,[3] whose results are summarized on pp. 33–34.

Absorption of Oxygen by Coal.

Winmill[4] has made further contributions to the study of the phenomena of low temperature oxidation and the spontaneous combustion of coal.

In one paper he considers the effect on the absorption, of the size of the coal particles, and the percentage of oxygen in the air in contact with the coal. Samples of coal from the Barnsley seam were broken up and graded by sieves. The rate of oxidation of the coal of different grades was measured by estimating the volumes of oxygen absorbed. Curves relating time and absorption were determined for periods of ninety-six hours. Winmill deduces that coal which passes a standard sieve of 200 mesh per linear inch has practically its maximum rate of absorption of oxygen, further subdivision being of little effect. The following table shows how particles of different grades compared when the relative surface and absorption rates of 200-mesh coal were both taken as 100.

—	Passing 200 mesh.	Passing 30, left on 60.	Passing 10, left on 30.	Passing 2, left on 10.
Approximate ratio of surface ...	100	20	7·5	1·7
Average ratio of absorption during the first 96 hours	100	80	72	27

[2] *Illinois Univ. Bull.* 76 ; *J.*, 1915, 213.

[3] *German Coke Oven Committee Report ; J.*, 1915, 895.

[4] *Trans. Inst. Min. Eng.*, 1916, **51**, Part 4, 484, 493, 500, 510.

Oxidation is therefore not regarded by the author as a simple surface action, although a small size of particle favours absorption.

In other experiments the rates of absorption of oxygen by coal from a number of oxygen-nitrogen mixtures containing from 5 to 100 % oxygen were measured. The rate of absorption was not simply proportional to the percentage of oxygen, but still the two were related. Winmill found the absorption rate to be proportional to the square root of the percentage of oxygen in the mixture used. The percentage of oxygen has on this basis to be reduced from the 20·9 (of air) to 5 before the rate of absorption is halved, and small reductions in the oxygen percentage have no considerable effect on the liability to spontaneous heating.

Winmill studied also the part played by pyrites. While with South Yorkshire coals pyrites is not, he finds, a determining factor, the oxidation of the coal itself being sufficient to account for spontaneous heating, some North Staffordshire coals are liable to fire, the coal-substance of which is not easily oxidizable. Pyrites may here be a determining factor. It must be remembered that the pyrites itself varies greatly in physical character. The hard brassy lumps of pyrites which seem to resist oxidation indefinitely obviously contribute in no way to the initial heating. In the North Staffordshire coals the pyrites is intimately mixed with the coal, black in colour, and readily oxidized.

The same author has made a survey of coals from several different fields, comparing their liability to fire with their avidity for oxygen, and other properties. Oxygen absorption was measured by passing pure air through coal-dust kept at a constant temperature, the air being analysed after passage through the coal. This was done at 30° C. and 60° C. to mark the variation with temperature. The influence of pyrites was also studied. Forty coals were examined, and fell into three main classes: (1) Anthracites and Welsh steam coals which have a small capacity for oxygen at 30° C., not appreciably greater at 60° C. These cannot fire spontaneously. (2) Coals with a low rate of oxidation, which increases with temperature. These are not normally liable to spontaneous combustion unless suitably mixed with pyrites. (3) Coals with a sufficiently large rate of oxidation to give rise to fires without the intervention of such a substance as pyrites. Classes 2 and 3 seem well differentiated. Coals not liable to fire usually absorb less than 200 c.c. oxygen per 100 grms. Oxygen absorption measurements, especially if made both at 30° C. and 60° C., seem, the author concludes, to afford a means of distinguishing between the different types. If the absorption is small, it cannot, however, be said that firing will not

occur unless the quantity and kind of pyrites has been determined and interpreted as already described.

The great and growing importance of preventing "spontaneous combustion" in stacked coal and in coal-mines is responsible for this work, which has been carried out at the Doncaster coal-owners' research laboratory.

Another aspect of comparatively low temperature oxidation of coal has been studied by Porter and Ralston,[5] who found that below 200° C. oxygen was absorbed with the formation of solid products and water, but that at higher temperatures carbon dioxide appeared.

The thermo-chemistry of coal decomposition during carbonization has received attention from Hollings and Cobb[6] (see p. 32).

A piece of work which should have been done long ago has been carried through by Fieldner[7] and collaborators, who have examined the influence of atmosphere on the softening temperatures of coal ashes under heat. These were depressed in mixtures of hydrogen and steam by the formation of fluxing ferrous silicate. An atmosphere of 50 % hydrogen–50 % steam was considered most suitable for comparative tests made on fifty coals. The highest temperatures were obtained for any given ash, when using an atmosphere of air, or one strongly reducing from carbon monoxide, which reduced iron to the metallic state (and not merely to ferrous oxide), prior to softening. The bearing of this work on gas-producer and general furnace practice is obvious.

Treatment and Use of Coal.

The satisfactory utilization of coal demands that its calorific and chemical values shall both be fully realized. Modern carbonizing processes do make use of coal as a raw material of chemical industry, and the urgent national needs for benzene, toluene, phenol, and dyestuffs have no doubt helped Bone,[8] Armstrong,[9] and others in their recent insistence that more must be done in that direction. Committees on fuel economy have been appointed by the British Association and the Society of Chemical Industry. It is to be remembered that coal, apart from its use as a reducing agent in the form of coke, is a source of heat (power and light), tar products, and useful nitrogen compounds, that each of these three factors of value is important technically and commercially, and that

[5] *U.S. Bur. Mines*, Technical paper 65; *J.*, 1915, 17.
[6] *J. Chem. Soc.*, 1915, **107**, 1106; *J.*, 1915, 862.
[7] *J. Ind. Eng. Chem.*, 1915, **7**, 399, 474, 742, 829; *J.*, 1915, 704, 1001, 1079.
[8] *Brit. Assoc. Rep.*, 1915. [9] *J.*, 1916, 220.

therefore no scheme for using coal can be regarded as ideal which does not promise good results in the three directions. The comparative merits of different attempts to approach that ideal are not usually to be estimated except with regard to special, often local, circumstances, and no doubt development will take place along several lines. Heat is wanted both in quantity and intensity for lighting and high temperature operations generally, but in quantity only for many other purposes; coke may be wanted hard or soft, tar suitable for different purposes, gas of high or low grade, ammonia always as far as is compatible with other requirements, and the coal must be treated accordingly. Low temperature carbonization may be expected to give a small yield of ammonia and very rich gas, with high yield of tar rich in low-boiling paraffinoid constituents, and a soft, easily burning coke, as referred to the standards of the higher temperature carbonization now usual in by-product ovens and gas works; gasification with air and steam on the Mond system offers a unique recovery of the nitrogen as ammonia, and very large volumes of clean but low-grade gas. Such processes solve, or attempt to solve, more or less completely, the problem of the rational use of fuel, and lead away from the wasteful direct burning of raw coal. Useful developments or combinations may be looked for, especially if the necessary progressive elimination of obvious waste is hastened by judicious legislation.

The open-coal-fire habit and standard steam boiler practice are mainly responsible for the continuing extensive use of raw coal. The former arises naturally from the custom of fitting all houses with grates which are only suitable for burning raw coal, a custom partially justified by the general æsthetic preference for the open fire, the high ash content of many cokes, and the price of gas. The latter has been strengthened in recent years by the more rapid development of the steam turbine as compared with the gas engine in large units, but the use of gas and coke as boiler fuel is beginning to receive more attention.

It is to be noted, too, that the employment of gas producers without recovery of by-products, although thermally satisfactory in conjunction with internal combustion engines or regenerative furnaces, is chemically as wasteful as either of the preceding.

Attention may be called to the manifest value attaching to any improvement in the methods of securing effective use for small coal and coke and for low-grade coals of high ash content. The problems are largely mechanical. A process[10] has been put into operation by the Simon-Carvés Coke Oven Co. by which the very finest coal from a

[10] Greaves, Priv. Commn.

washing plant, after passing through a sieve and settling somewhat, is returned from the bottom of the settling vessel and is finally filtered through the coarser coal, so effecting that intimate mixture with the coarser coal which is necessary for practical utilization in the coke-oven.

There has been little change in by-product coke-oven work in general, attention having been largely concentrated on labour-saving devices. Progress has been reviewed by Lishman.[11]

Many benzol plants have been put down for producing washed and rectified 90 % material, while some coking installations go still further and make the pure products. Steam is almost always used in these plants, but recently Wilton[12] has patented and installed apparatus for the production of crude 65 % naphtha by direct firing. The process is carried out by pumping the benzolized wash oil through coils heated by direct fire. The benzolized oil is kept in the coils under a pressure and temperature sufficient to ensure that the benzene and toluene leave the wash oil when the pressure is relieved in a dephlegmating still. No steam is used for the distillation of the wash oil, and fuel is therefore saved; water is thoroughly eliminated from the wash oil.

The use of coke-oven gas for town supply has been recently adopted by Leeds, following Middlesbrough. One million cubic feet per day is piped from the Middleton Coke Ovens to the Leeds gas system.

Bergius,[13] who has previously published the results of work on the artificial formation of coal from cellulose under the combined influence of high pressure and moderately high temperature, and on the preparation of hydrogen from water under similar conditions, has extended his method to the treatment of coal. In this process coal is heated to a temperature from 300° to 350° C. with hydrogen or hydrogen mixtures under pressure, preferably above 100 atmospheres. The hydrogen, it is claimed, reacts readily, giving liquid products (at ordinary pressure and temperature), or low-melting solids, without the production of non-condensible gases, nitrogen being recovered as ammonia. The use of such a solvent as petroleum distillate is said to be helpful. The costs of installation, working, and upkeep of the plant for this process would be of interest, but are not available.

In another patent, Bergius[14] claims the application of his process to coal distillation products such as tar and pitch. He states as exemplifying its results that one kilo of tar, heated with hydrogen to 400° C.

[11] *J.*, 1916, 767.
[12] Greaves, Priv. Commun.
[13] Eng. Pat. 18232 (1914), *J.*, 1916, 167.
[14] Eng. Pat. 5021, 1915, *J.*, 1916, 732.

at 100 atmospheres pressure for four hours and afterwards distilled at 250° C., gave about 60 % of distillate resembling petroleum oil.

Liquid Fuel.

The subject of mineral oils is treated fully in a separate section (pp. 61–66), in which the work of Rittman and his collaborators[15 16 17 18] is considered.

In view of the shortage of mineral oil, Moore[19] has called attention to the possibilities of coal tar and its constituents, especially creosote oil, as fuel for engines of the Diesel type. Tars for Diesel engines should have, according to this author's standards, high hydrogen content (due to aliphatic hydrocarbons), low free carbon, high calorific value, low viscosity, less than 2 % water, less than 15 % coke value, and less than 0·15 % ash. Low-temperature carbonization is favoured for the production of such tars.

The use of naphthalene as a source of liquid fuel was the subject of a patent by Sabatier and Mailhe[20] in 1914, according to which hydrogen and naphthalene vapour are passed over a catalyst (metallic powder or alloy), when liquid hydrocarbons are formed. In all probability current need has stimulated many experiments in this and similar directions with results outrunning publication.

Another process for the same purpose has been described recently by F. Fischer,[21] who states that in his experiments commercial naphthalene was heated under pressure in an autoclave for 20 minutes with 4 % aluminium chloride at 330° C. It yielded about 33 % of liquid, the greater portion of which distilled between 150° and 300° C., and after removing naphthalene from the distillate 18 % of liquid was left. It is suggested that this product is something between naphthalene and dihydronaphthalene and that possibly part of the naphthalene is hydrogenized at the expense of the other part.

The direct use of naphthalene as a motor fuel is the subject of an article by Bruhn.[22] He discusses those chemical and physical properties of naphthalene which enable it to be used in the molten condition for internal combustion engines after the engine has been once started,

[15] Rittman, *Bur. of Mines*, Bull. 114.
[16] Rittman and others, *J.*, 1916, 105, 169.
[17] Egloff and Moore, *Met. and Chem. Eng.*, 1916, 67; *J.*, 1916, 882.
[18] Rittman, Byron and Egloff, *J. Ind. and Eng. Chem.*, 1915, **7**, 1029; *J.*, 1916, 105.
[19] *Manch. Assoc. Eng.*, Feb. 26, 1916; *J.*, 1916, 345.
[20] Fr. Pat. 477212 (1914), *J.*, 1916, 628.
[21] *Ber.*, 1916, **49**, 252, *J.*, 1916, 350.
[22] *J. Gasbeleucht*, Nov. 2 and 9, 1915; *J.*, 1916, 165.

and estimates that from 1911 to 1913 the aggregate horse power of naphthalene engines increased from 678 to 3934. The cost per h.p. hour is claimed to be much lower than that of petrol or benzol engines.

Gaseous Fuel.

The more scientific study given in recent years to the use of coal gas as a heating agent and to the design of apparatus for the purpose, the realization that producer gas, especially with by-product recovery and concomitant cleanliness, is much more effective than raw coal in so many processes, the increasing use of the gas engine, and the growing necessity in America for independence of the lessening supply of natural gas, are combining to increase the amount of investigation given to the enormous potentialities of gaseous fuel.

The manufacture of coal gas receives attention in another section.

Producer Gas.

Alteration in the design of gas producers is developing chiefly in attempts to discard hand pokering, to provide an even bed of fuel, and to minimize labour. The mechanical type of producer installed by the Power Gas Corporation has a revolving central poker with projecting arm, which sweeps through the upper layers of the fuel bed. The formation of caked lumps, and channels, in the coal with consequent irregular distribution of the ascending gas current, and lowered quality of the gas at the top of the reducer, is so prevented. The poker is a simplification of the older form of Talbot poker, to which a lower arm was attached revolving in the clinkering region of the fuel bed.

Another problem is attacked in the revolving stepped "Teesside" grate; the lower half of the producer case consists of water-cooled iron with no firebrick lining; both features of construction aim at facilitating the breaking-up and removal of ash.[23]

In the Morgan producer[24] a rotating ash-pan moves past a stationary blade fixed on the producer. The upper part of the producer dips into an annular water seal and is stationary, while the lower part of the casing is rotatable. Another type[25] is so arranged that the fuel bed is not poked or disturbed. Fuel is supplied in small quantities automatically, and the surface of the fuel bed is levelled continually by a water-cooled leveller of |_| section "floating" on it. The bottom of the producer is swept

[23] Beswick, *Priv. Commn.*

[24] Morgan, U.S. Pat. 1142100 (1915), *J.*, 1915, 787.

[25] *Met. and Chem. Eng.*, 1915, 399

by a spiral-shaped bar or plough, the result claimed being a uniform settling of the ash over the entire area. Great claims are made for this design in labour saving, output and quality of gas.

Stein et Cie[26] have protected a revolving grate with teeth projecting both inwardly and outwardly, the axis of rotation of the grate being eccentric to that of the producer.

Verson[27] describes a producer provided with a vertical shaft carrying a rotating block with helical ribs surrounded by a member also having helical ribs. The descending cinder is broken up in the tapering space thus formed. The gas receiving chamber is disposed near the combustion zone. An interesting combination of what is essentially a gas-retort and a producer is patented by Mastaing and Monnier.[28] The producer has a central open core. The retort above, which also acts as a feed chamber for the producer, is surrounded by flues leading from this central core. The producer is started up on coke, and in order to attain the temperature required (1100°–1300° C.) for coking raw coal in the retort-hopper, part of the producer gas is burned in the central core. The coke in normal working is dropped into the producer from the retort. The gas drawn off is a mixture of coal gas and producer gas; its calorific value is said to be about twice that of ordinary producer gas, and the tar to resemble that from ordinary coal gas retorts.

The constructional difficulties of any such arrangement as has been described are obvious, and if the combined retort-producer in any form is to succeed, skilful design will be imperative to meet working conditions.

Further attempts are being made to destroy in the producer the tar formed by distillation of the coal. Thus the Chapman producer[29] is described as made in three sections, two, at top and bottom, revolving and the central one stationary. Gases evolved from the raw fuel are withdrawn and fed into the incandescent material in the stationary section.

Carrey[30] protects another design.

The inherent difficulties of destroying tar, and the very short time of contact with red-hot carbon possible in a gas-producer, account for the want of practical success hitherto attained in this direction. The claim for destroying tar[31] put forward by early advocates of the Mond

[26] Fr. Pat. 473932 (1913), *J.*, 1915, 787.
[27] Eng. Pat. 24329 (1913), *J.*, 1915, 825.
[28] Fr. Pat. 469967 (1914), *J.*, 1915, 71.
[29] U.S. Pat. 1125962 (1915), *J.*, 1915, 268.
[30] Carrey, U.S. Pat. 1176429 (1916), *J.*, 1916, 592.
[31] Humphrey, *Proc. Inst. Civ. Eng.*, Mar. 16, 1897.

system (quite unnecessarily in view of its many excellences), has not been justified. The construction of the producer, the low temperatures prevailing in any part of the fuel-bed which the tar can reach in normal working, and the speed of the gas currents ensure, as a matter of fact, the production of a low-temperature paraffinoid tar, and a minimum of exposure to decomposing influences.

Stahl und Eisen,[32] dealing with the immediate necessity for coking as much coal as possible, asserts that certain ironworks have used small coke mixed with coal in gas-producers, and have also experimented with coke alone. The average of sixteen analyses of gas on different days shows the gas composition as below :

50 % coal } CO_2 1·5, CO 29·3, H_2 7·2, CH_4 3·0, N_2 59·2 %.
50 % coke } Heat value, 1323 Cals. per cu. m.
Coke alone :—CO_2 2, CO 29·4, H_2 6·7, CH_4 1·7, N_2 60 %.
Heat value, 1202 Cals.

The use of peat in gas-producers is largely rendered possible by the high ammonia recovery which is practicable in plants of the Mond type. Rossi[33] gives particulars of an Italian installation operated since 1910 ; 175 lb. of ammonium sulphate is made per ton of peat from peat containing 2·5 % nitrogen.

The contained moisture is usually a trouble with peat, and Haanel,[34] reviewing the subject, believes that the maximum moisture permissible for efficient utilization is under 40 %, and that by-product recovery should not be attempted if the nitrogen is below 1·5 % in the dry material. Special circumstances may, of course, make any such standard inapplicable.

The International Nitrogen and Power Co.[35] propose to feed the peat into an airtight hopper above the producer, heated by hot gases from the producer passing through a concentric outer tube. Moisture is drawn off from the peat and delivered with the air at the producer hearth. The peat is fed to the producer by a rotating worm.

As a rule the complications and irregularities in working which come from the ash in coal are met nowadays by the free use of steam, which keeps down the temperature in the fuel-bed, prevents the formation of clinker, and, moreover, is essential for ammonia recovery, but the

[32] *Stahl und Eisen*, 1915, **35**, 507 ; *J. Iron and Steel Inst.*, 1915, **2**, 251.
[33] *J. Roy. Soc. Arts*, 1915, **63**, 162 ; *J.*, 1915, 130.
[34] *Canada Dept. Mines*, Mines Branch, 1914, Rep. 299 ; *J. Iron and Steel Inst.*, 1915, **2**, 250.
[35] **Eng. Pat. 476 (1914), *J.*, 1915, 268.**

exactly opposite plan is still sometimes followed. For this purpose the producer is worked with no steam, so as to secure maximum temperature in the fuel-bed, and to run off the ash as a liquid slag. The producer must be of special design and the composition of the coal-ash suitable or modified by additions. Paul Würth & Co.[36] have extended a plant of this kind, and claim good results. In it small coke is used, with a consumption of 60 tons per producer per day, making gas containing 34 % carbon monoxide, with only 1–2 % carbon dioxide and a heating value of 1200–1350 cals. per cub. metre. The iron oxide in the cinder is said to be reduced and recovered on tapping the slag as a high-silicon, low-sulphur pig iron.

In a general review of American producer-gas practice, Kline,[37] at the International Engineering Congress, San Francisco, 1915, points out that producers are growing in popularity as natural gas becomes scarcer and oil more expensive, and that development has been toward mechanically operated plants and towards fixing the tarry constituents of bituminous coals. He says that at last manufacturers are realizing that a gas-producer plant cannot be run without competent men and appliances for checking the quality of gas and temperature control.

Working results for Mond, Kerpely, Dowson and Mason, Kynoch, Cambridge, and Duff, producers in this country, have been given by Mills,[38] who also discusses the availability of seams of coal unsaleable at the present time.

Ammonia Yield.

The conditions of maximum ammonia yield from coal gasified in producers have received considerable attention lately. The ammonia is obviously to be first generated and then preserved. The Mond process, in which air saturated at 85° C. with water vapour is used in the gasifying of coal, is successful to the extent of giving 60–70 % return of the nitrogen in the coal as ammonia, but the process demands the passage of a large quantity of undecomposed steam through the producer, and imposes supplementary plant of some size and complication for securing thermal economy. The important question arises as to how far the same object may be attained in other ways, and the favoured plan seems to be the placing of cooling surfaces to prevent destruction of ammonia by heat. This may call for complicated design, and its working out in large producers is no easy task, involving, as it presumably will, the use of internal coolers in the producer.

[36] *Stahl und Eisen*, 1914, 1135; *J. Iron and Steel Inst.*, 1915, **1**, 528.
[37] *Met. and Chem. Eng.*, 1915, 728. [38] *Trans. Inst. Min. Eng.*, 1915, **1**.

The Moore[39] producer is made with an annular jacket, which is in effect a boiler and a gas-cooler, but one with small surface and in contact with the outer edges only of the main gas stream. It is claimed that, with an ammonium sulphate recovery of 90·5 lb. per ton of coal, the weight of steam used was 1 ton per ton of coal, half of which was generated by the annular boiler. The gas analysis quoted is:—

CO_2 11·6, CO 18·4, H 26, CH_4 2·2, N 40, water vapour 1·8; total combustibles 46·6 %, a high standard to maintain.

The recovery as given is up to Mond standard, and the steam supplied from outside sources ½ ton as against 1½ tons.

An article[40] in *Glückauf* also deals with a water-jacketed producer. The ammonia formed is said to be protected from decomposition by the chilling of the producer above the combustion zone. There are three zones in this producer, the uppermost being air-cooled, with a mean temperature of about 180° C. The second is water-cooled, and has a mean temperature of 300°–450° C., while the temperature of the combustion zone is 800°–1000° C. It is stated that as soon as a temperature of 450°–500° C. is reached further protection of ammonia by excess of steam is unnecessary, so that only sufficient steam to produce the ammonia is used. The gas is air-cooled, and ammonia is recovered as ammonia liquor in two scrubbers.

On the same subject Sachs,[41] in addition to laboratory experiments, has made tests on a suction gas-producer. He finds the yield of ammonia to increase with the amount of steam supplied, and that, using relatively small quantity of steam, 900° C. is the best working temperature, but with a large quantity of steam 800° C. His experiments show that a sudden cooling of the reaction products results in increased yield of ammonia, and it is stated that results superior to Mond process working can be obtained on a large scale. With a large quantity of steam the whole of the nitrogen can be converted into ammonia, and this is held to confirm the view of Rau and Christie[42] that nitrogen in coke is present as a carbon nitride.

According to experiments by Salmang,[43] the combined hydrogen in coke plays no part in the formation of ammonia during the gasification process. With steam and air at 900° C., 59 % of the nitrogen is converted to ammonia, while with steam alone at 1050° C. (water-gas process) 36 % is converted. In both cases the yield is said to be

[39] See *Engineer*, 1915, 326.
[40] *J. Gas Lighting*, 1915, **130**, 638.
[41] *Stahl und Eisen*, 1915, **35**, 801; *J.*, 1916, 346.
[42] *Ibid.*, 1910, **30**, 1235, 1282.
[43] *Ibid.*, 1915, **35**, 905; *J.*, 1916, 346.

increased materially by addition of 5 % of lime, up to 96 % of the theoretical in the mixed gas process, while ferric oxide acts in the same direction, but in a lesser degree. The ammonia formation is stated to progress uniformly during the combustion of the coke.

Ammonium Sulphate.

For producer plants making ammonium sulphate, the past year has been difficult owing to the scarcity and high cost of sulphuric acid. An effort has been made in this country to raise the standard ammonia content to 25 %, not an easy matter where the ammonia is not redistilled into acid, but by careful washing and drying the ammonia content has been substantially increased. The proposed substitution of nitre-cake for acid can only be made in quantity at a substantial expense in purity of the ammonium sulphate, apart from the danger to lead work from any nitric acid left in the nitre-cake. Laboratory experiments[44] showed that when 2½, 5, 10, and 15 %, in turn, of the sulphuric acid for making ammonium sulphate, was supplied as nitre-cake, the crystals, obtained on evaporation to semi-solid, filtering hot, were of the (dry) composition below :—

—	2½ %	5 %	10 %	15 %
Ammonia	25·24	24·51	21·76	19·89
Ammonium sulphate	98·02	95·17	84·08	77·22
Sodium sulphate	0·81	3·51	14·04	20·82
Free acid	0·87	1·20	0·80	0·75

Further laboratory experiments indicated that in a liquor, such as that circulating in a Mond recovery plant, the ratio $\frac{\text{sodium sulphate}}{\text{ammonium sulphate}}$ was the same in the crystals removed and in the mother liquor, when 10 % of the sulphuric acid used was replaced by equivalent nitre-cake.

The sulphuretted hydrogen in the gas obtained from coal by complete gasification in producers, or by carbonization, contains usually sulphuretted hydrogen more than equivalent to the ammonia present. Ammonium sulphide can therefore be regarded as available, and if the direct or indirect oxidation to ammonium sulphate can be made, no sulphuric acid need be supplied from outside. For some years several forms of the Feld and Burkheiser processes for this purpose have been under trial. Another process has been recently put forward by Cobb[45] ;

[44] King, *Priv. Commn.*

[45] Eng. Pat. 13141 (1912), *J.*, 1913, 971.

the gas is washed with a solution of zinc sulphate, which gives the ammonia at once as ammonium sulphate solution, and the sulphur as precipitated zinc sulphide. On roasting in air the latter forms sulphate and oxide, and the sulphur oxides, given off along with excess air, are blown through water, in which is suspended the solid residue from a previous roasting. The zinc sulphate solution so regenerated is used again. The process is being tested on the working scale.

Purification of Producer Gas.

The practice of washing producer gas and recovering ammonia from it is differentiated from that in use at coke-ovens and gas works by the necessity for dealing with more than ten times the volume of gas per ton of coal gasified, and, usually, large quantities of steam.

A full description, with drawings and photographs of a new washing plant due to Lymn, is given in *Engineering*.[46] It consists of vertical cylindrical chambers, each containing fixed inverted truncated cones, and revolving horizontal discs mounted on a vertical shaft. The spinning throws a spray of water, or liquor, from the revolving discs to the cone. The ascending producer-gas is thus washed by a series of liquid films. In another pattern, stationary discs are used, the claim being made that the momentum of the ascending gas obviates the necessity for the revolving discs.

The electrical purification of gas has been described by Smith,[47] according to whose process the gas is passed through a diaphragm of glass wool at such a speed that the fibres are electrified, when the particles of tar coalesce and are removed by the glass wool or by another filter. Howl and Perry[48] have described an application of the electrical method to power gas. For the removal of tar or tar fog the gas is passed up a vertical metallic tower, the lower end of which is an insulated water tank, which has means of producing a fine water spray in the tower. The water tank is connected to one pole of a high voltage machine, and the base of the tower to the other pole. It is found better to have the water spray charged negatively.

The behaviour of explosive gas mixtures is of interest and has been investigated by W. M. Thornton,[49] who concludes from his experiments on mixtures of air with a number of combustible gases that the electrical ignition of such mixtures is "stepped," *i.e.*, when the

[46] *Engineering*, June 4th, 1915, 624.

[47] Smith, Fr. Pat. 472396 (1914), *J.*, 1915, 414.

[48] *J.*, 1915, 483.

[49] *Proc. Roy. Soc.*, 1914, **90**, 272; **91**, 17; 1915, **92**, 9; 1916, **92A**, 381; *J.*, 1916, 682.

composition of a given mixture is gradually altered, the spark energy required to ignite it is characterized by sudden changes. Sastry,[50] however, fails to confirm this, finding that the spark energy varies continuously with the composition of the gas mixture from the lower to the upper limit of explosion. It seems here advisable to wait for a more unquestioned establishment of the basal facts before dealing with theoretical speculations arising out of them.

Gas Heating.

The use of coal-gas from retorts, and similar high-grade gas for industrial heating processes, has been increasing very rapidly during the period under review, because of the necessity for rapid installation, control of temperature and atmosphere, and in many cases absence of grit and dirt. The experience so gained will probably allow this heating agent to take its proper place, especially if a more enlightened public policy insists upon the price of gas being governed by economic wisdom rather than political opportunism, and if statutory restrictions as to quality are determined by living instead of historical influences.

Even with existing prices the higher thermal efficiency and output realizable with gas have demonstrated the economy of its use for many purposes. The Richmond and Brayshaw companies have been prominent in this work, and the Birmingham Corporation Gas Department has successfully extended its applications of high-pressure gas and gas-heating generally.

Industrial Appliances.

Most of the developments in this branch which have taken place during the last two years have been connected with the production of war material. Thus, an appliance similar in principle to the domestic gas cooker, but of course considerably larger in size, has been adopted for the drying of shells after the varnishing process. These ovens are made of the externally heated type, owing to the fact that the introduction of a large mass of cold metal into the internally heated oven involved the condensation of water, and a consequent rusting on the outside of the shells.

Gas-heated furnaces are used to a considerable extent in connection with various processes in the manufacture of shells and gunfittings. The adoption of gas as a fuel has rendered easy control of the temperature possible, and uniform temperature throughout the furnace obtainable with a consequent improvement in results. In addition, there is a marked saving in labour and space.

[50] *J. Chem. Soc.*, 1916, **109**, 523; *J.*, 1916, 682.

Annealing, etc.

Low pressure gas furnaces are constructed to work with natural draught, or with air at a low pressure, for case-hardening and annealing. The low pressure gas and air furnace has been made in some very large sizes.[53]

A gas furnace for this process has been developed on the lines of the solid fuel fired reverberatory furnace, in which a large body of heat at a moderately low potential was available, and these conditions are now obtained by causing moderately aerated flames from ordinary atmospheric burners to envelop the work to be annealed, and by conserving as much as possible of the heat of the waste gases by passing through regenerator flues arranged in the massively constructed furnace bed. Provision is made for controlling the amount of secondary air used for combustion, with the result that the furnace can be run, if necessary, with a slightly reducing atmosphere, and thus oxidation of the work is eliminated. In some designs, secondary air is admitted under a slight pressure of about 6 in. W.G., and this is found to be very satisfactory in the case of annealing large quantities of steel, the time required for heating up the furnace to the working temperature being considerably less than when atmospheric burners are employed. For town gas of a nett cal. value of about 500 B.T.U. per cubic foot, the average gas consumption per lb. of metal annealed, including gas used for preliminary heating of furnace, is given as:—[54]

Nature of work.	Gas consumption in cub. ft. per cwt. metal annealed.
Light brass stampings	100–125
Heavy brass stampings	150–200
Light iron and steel stampings	150–200
Heavy steel stampings, dies, etc. ...	200–300

A variety of blast furnaces is employed in the tool room for the preheating and final hardening of all types of milling, lathe, and boring tools. These furnaces work with gas and air blast, and are capable of giving very high temperatures; 1300° C. and, if desired, considerably higher temperatures, can be obtained, it is claimed, in about twenty to thirty minutes after lighting up. Salt bath, lead, and oil tempering furnaces for dies, cutters, etc., are also in work.

[53] Hartley, *Priv. Comm.*

Carburizing.

During the last few months experiments have been made in the Industrial Heating Laboratories of the City of Birmingham Gas Department, on the carburizing of mild steel in a coal gas atmosphere,[52] the work being placed in a vertical retort composed of refractory material, with its lower end sealed in the quenching medium, which may be water, oil, or molten metals. The retort is heated externally by means of a small gas furnace of the cyclone pattern built round it, and the work is suspended within the retort through which town gas is passed, the gas having been previously bubbled through an aqueous solution of ammonia. This process is now being used commercially with every success, and small parts of instruments, axles, small tools, and gauges are being produced by this process with a minimum of distortion and surface decarburization. A modified form of the same design of furnace is also being used in connection with the heat treatment of carbon and alloy steels.

Work on this subject has also been done by White and Hood.[53]

Melting of Copper, Brass, Aluminium, etc.

The application of town gas for the melting of copper, brass, bronze, gunmetal, and aluminium has made considerable progress during the past twelve months, the systems most commonly employed being either an air-gas system with gas at a pressure of about 2 in W.G., and air under a pressure of 2 lb. per square inch, or gas at a pressure of about 12 lb. per square inch. Many full-scale tests have been made in order to determine the relative values of each system, and the results obtained show that where large quantities of metal can be quickly handled, as in the case of melting scrap metal for casting into ingot, the air-gas system shows a saving in fuel cost as compared with the high pressure gas system, but the cost of maintenance of linings is found, in most cases, to be considerably greater. In the case of cabinet and offside work, where 60-lb. pots are employed for casting metal into sand moulds, taking the overall cost of melting, including fuel cost, pot cost, maintenance of furnace linings, burner repairs and metal loss, depreciation of plant, labour charges and standby losses, the high pressure gas furnace is found to be the more economical, and at the same time has the advantage of simplicity of control. The opinion at the present time with regard to the relative advantages of the high pressure gas and air-blast systems is somewhat divided, but experiments carried out on a full scale with both systems show conclusively that

[52] *J. Gas Lighting*, 1916, **134**, 691. [53] *Ibid.*, 1915, **132**, 312.

each system has its advantages according to the particular melting process under consideration.[54]

An appliance which promises to be useful wherever it is necessary to maintain unaltered, during the heating, the ratio of gas to air is due to Ionides[55]; it is known as the pressure balance, and consists of a chamber enclosing a floating bell, with gas inside and air outside the bell, which rises and falls with any altering pressure of gas or air, and operates both the gas and air supply through attached valves, in the direction of maintaining the original proportion. The appliance seems simple and effective, and very good results are claimed for it in melting and heating metals with town gas. It is to be tried for producer-gas.

A useful general review of the uses of coal gas for industrial purposes has been made by Thornton.[56]

Heating by producer-gas has found numerous applications, principally in connection with chemical works, in the generation of power for electrolytic plant, the heating of sulphonating pots, nitric acid stills, sulphuric acid concentrators and caustic pots, and for distilling and evaporating liquors, tar, and oil. A Mond plant has been extended and fitted with purification plant to supply gas to engines for the generation of 11,000 brake horse power to be used in electrolytic work. The Tottenham District Light, Heat and Power Co. is installing external water-cooled gas-producers with rotating grate (Tees type) for the automatic removal of ash, and it is intended to gasify coke breeze and generate gas for firing a battery of vertical retorts.[57] A mixture of breeze and coal is in use at the Birmingham Corporation gas-works for heating coke-ovens, the fuel being gasified successfully in Mond producers with ammonia recovery. The possibilities in this direction for the coal-gas and coke-oven industry, particularly in large plants, are probably very great.

Small gas-producers of the suction type, in which the use of anthracite, coke, or charcoal minimizes tar and other troubles, have also come into extended use.

Domestic Heating.

The tendency to minimize unnecessary domestic work, and the successful results attending the scientific study of the gas fire, have combined to extend the use of gas for domestic heating. Some years ago, when the Gas Heating Research Committee of the Institute of Gas Engineering and the University of Leeds commenced its work, the

[54] Walter, *Priv. Comm.*

[55] *J. Gas Lighting*, 1915, **129**, 380.

[56] *Ibid.*, 1915, **129**, 717, 743.

[57] Beswick, *Priv. Comm.*

gas-fires of the day radiated only from 35–42 % of the nett heat of combustion of the gas burned in them; 50 or 55 % would now be more typical. Undoubtedly the intelligent use made by the gas-fire makers of the method then introduced for determining the percentage radiant efficiency has contributed to this result.

The method consists in observing the relative intensity of radiation at a number of points (eighty-one in all) on an imaginary hemisphere enclosing the fire tested, and combining the result so obtained with absolute determination of the radiant heat falling on a single unit of area of the hemisphere. The relative intensities have usually been taken by a thermopile, originally by a Rubens Linear Thermopile, but Callendar has designed a new form of bolometer, the use of which has been described.[58] This bolometer consists of two exactly similar blackened coils, each 0·7 inch square and of 20 ohms resistance at 20° C., mounted back-to-back in a circular box, but separated by a chamber through which water at room temperature can be passed. The removal of a cap exposes one coil to the radiation, with consequent rise in resistance.

The absolute measurement of radiation has usually been taken by the R. H. Smith radiometer, in which the radiant heat falling on a square foot of blackened copper tubes facing the fire is measured by the rise in temperature of a measured quantity of water flowing through the tubes. Another method of carrying out this part of the test has been described by Hartley,[59] who determines the rise in temperature of a block of brass exposed to the radiation. The block is 6 inches square, and usually $\frac{3}{4}$ inch thick, blackened on the exposed side and polished on the others. The temperature is measured by a thermometer fitted into the block, and convection currents are minimized and regularized by enclosing the block in a water-jacket with one open side, which exposes the blackened surface only to radiation. Callendar's radio-balance is also suggested for the absolute radiation measurement.

Whatever the measuring instrument used, the advantages of the method just described are that the distribution of radiant heat, as well as its total, is determined—a matter of increasing importance as design is improved—and that, as compared with an alternative method, which consists in measuring calorimetrically the whole of the radiation from a fire by absorbing it on an enclosing hemisphere, it is much less liable to the error of counting convected and conducted heat as radiant.

In a modern gas-fire half the heat of combustion may be taken as

[58] Bone, Callendar, and Yates, *Proc. Roy. Soc.*, 1915, A, **91**, 245–254; *J.*, 1915, 415.

[59] *J. Gas Lighting*, 1915, **129**, 794.

radiated, a quarter as going away in the flue gas, and the remaining quarter as dissipated for the time being (but not necessarily lost) by convection and conduction. The fractions are approximate. The heat in the flue gases is responsible for the ventilating effect of the fire, and recent experiments by the Ventilation Research Committee of the University of Leeds and the Institute of Gas Engineers have shown[60] that even modern fires differed materially in the extent to which this heat was utilized as an air-moving force, and that the use of auxiliary air-inlets could effect marked improvements in this respect. The gas-fire is developing in the direction so indicated.[61]

The lowered temperature in the flue, which results from increased air removal by a gas-fire, necessitates, however, care to avoid down draughts, and some experiments on this subject are described in the third report of the committee mentioned above.

Another marked improvement in the gas-fire has been the complete elimination in all the best types of any escape of products of combustion past the canopy into the room. The escape can be easily tested by the method of the Ventilation Research Committee, which determines the addition of carbon dioxide to the air rising in front of the canopy. A rapid and ocular demonstration of escape may be obtained by the *Lancet* method, according to which carbon tetrachloride is injected into the primary air-supply; the deposition of moisture on a bright, cool metal surface has been employed for the same purpose.

Other improvements have been directed to silencing the flame by improving the mixing, and eliminating objectionable eddies, in the primary air and gas.

Hot plates, boiling burners, and water-heaters have also received attention. The practical limit of efficiency for low-temperature processes, such as water-heating, is partly determined by the necessity for avoiding excessive condensation of products of combustion, with consequent corrosion, arising from sulphur compounds remaining in the gas. This necessity may no longer exist if such a process as the Carpenter-Evans comes into general use.

Surface Combustion.

The special method of heating depending on surface combustion (accelerated combustion of gaseous mixtures due to their contact with surfaces) is mentioned below in connection with steam boilers. For large high-temperature furnaces the method seems to have one

[60] *Reports of the Ventilation Research Committee: Trans. Inst. Gas Eng.*, 1914, 1915, 1916.

[61] Hartley, *J. Gas Lighting*, **124**, 513.

inherent weakness, since it is a recognized feature in the design of such furnaces that the exposure of the refractory material of the furnace is to be minimized, and therefore any system which depends on deliberately generating the highest temperature among the refractory material imposes a new necessity in the provision of that material in quantity and in a superlatively resistant form. Where, however, the heat generated so rapidly by surface combustion is very quickly radiated, conducted, and used, as in steam boiler tubes packed with refractory material, the temperature need not rise unduly, and it is not surprising that this is the direction in which application of surface combustion to large-scale work has been made. Reverting to large high-temperature furnaces, the generation of high temperature therein involves usually the principle of continuous recuperation, or regeneration, with reversals, and is accomplished satisfactorily, but it depends upon a transference of heat from the products of combustion through an intermediary solid to the gas and air. This process is comparatively slow, and although it can be effected readily in the times of contact allowed in large furnaces, it is too slow for the times permissible in small-scale working. Hence the unsatisfactoriness, for instance, of laboratory regenerative furnaces; hence also that necessity for independence of the regenerative principle in small high-temperature appliances which is met by the use of high-grade gas; it affords an opportunity for such a process as that of surface combustion, but difficulties with temperature distribution and the refractory material remain, and may be responsible for the small progress reported in this direction.

The diaphragm form of surface combustion appliance, in which gas and air maintain the surface of a porous diaphragm of refractory material at high temperature with no issuing flame, is said to be working successfully and economically for evaporation in sugar factories.

Steam Boiler Practice.

The steam boiler and engine remains the standard combination for the generation of power, and as such demands separate treatment. Increasing fuel cost is emphasizing the necessity for scientific control, such as is only to be secured by examination of the fuel, particularly as to its calorific value, analysis of the flue gas, simplified by the introduction of carbon dioxide recorders in good working form, and checks on temperature, now easily obtained by the use of the thermocouple.

Coke, low-grade fuel high in ash, and coal dust, all provide their special problems in the way of boiler design, more particularly furnace design, if they are to be employed effectively. The use of gas, both low and high grades, for steam raising, is spreading, and will spread

further, as by-product extraction takes its proper place in the scheme of fuel utilization, unless the internal combustion engine intervenes.

As concerns the use of coke, no difficulty as regards percentage thermal efficiency realizable in practice would be expected, or exists, and coke has been used successfully in the past to a very considerable extent in grates of special design with forced draught. The substitution of coal by any considerable percentage of coke in a boiler furnace designed to use coal alone is naturally attended by some lowering of output per unit of grate area, but this only emphasizes the necessity for carefully considered modification in construction.

Under this head, Nichol[62] points out that boilers are now designed for use with coal containing full proportion of volatile products, more or less provision being made for the prevention of smoke. He recommends that for use with coke the grates should be raised nearer to the boiler tubes, that the fire-grate should slope upward toward the back end to ensure efficient cleaning, and that long and complicated flues and baffles should be simplified. He regards improvements in the circulation of water as necessary owing to the localized radiant effect from coke as compared with long-flaming coal. The same author[63] has published a comparison of results favourable to the use of coke, obtained from a bituminous coal and a gas coke when the former was burned by natural draught and the latter by forced draught, under similar boilers. The evaporation given was 6·83 lb. of water from and at 212° F. per lb. of coal as against 8·74 lb. for coke, and the nett thermal efficiency 70·7 % for coal as against 85 % for coke (deducting 3 % for steam used in the blower).

A detailed report from Germany[64] claims very good results for a mixture of equal parts of coke and coal. With coke alone the steam pressure was not so easily maintained, but the firing and grate-cleaning were not attended by any difficulty. The smoke nuisance was nearly eliminated by using the mixture, even with smoky coal. The trials were on ordinary firegrates, and it is thought that even better results would be obtained with specially designed grates. A report to the German Home Office[65] states that coke is found unsuitable for use with mechanical stokers, but can be burned on ordinary hand-stoked grates. The coke should be in small pieces, with high porosity, low mechanical strength, ash, and water content. When mixed with coal

[62] *J. Gas Lighting*, 1915, **129**, 269, 447.
[63] *Ibid.*, 1916, **133**, 695; *J.*, 1916, 460.
[64] *Glückauf*, 1916, **52**, 25; *J. Iron and Steel Inst.*, 1916, **1**, 315.
[65] *Braunkohle*, 1915, **14**, 255; *J.*, 1916, 345.

the best results are said to be obtained with a mixture of 20 % porous gas coke and 80 % of highly bituminous coal.

Herring[66] gives average figures for eight years as obtained from Lancashire boilers fired with coke breeze. The evaporation was 7·35 lb. of water per lb. of coke breeze.

Clement, Frazer, and Augustine,[67] of the U.S. Bureau of Mines, on a more general subject, describe experiments with a furnace having an exceptionally long combustion chamber. It is shown that with a constant rate of firing the time necessary for the complete combustion of the gases decreases with increasing air supply.

A highly specialized type of gas-firing for steam raising is exemplified by two Bonecourt surface-combustion boilers which have been installed in a Midland ironworks, primarily to provide steam for producers. Before entering the producers the steam passes through turbines which drive fans to provide draught for the boilers. In the turbines the steam pressure falls from 80 lb. to 3 lb. per square inch. The boilers are constructed with 36 tubes of 6 inches diameter, each boiler being 10 feet in diameter and 12 feet long, while the total internal heating surface is 715 sq. ft. The evaporation, from and at 212° F., is given as 21 lb. per sq. ft. of heating surface per hour.[68]

In a surface combustion boiler the gas burns among pieces of refractory material with which the tubes are packed, and the refractory material radiates and conducts heat to the tubes. The arrangement has been adopted without surface combustion by packing the tubes of a boiler with pieces of refractory material for absorbing heat from the exhaust of a gas engine.

Dust Firing.

The importance of appliances for burning very small coal arises from the necessary production of considerable quantities of this material in coal mining. It lies too close in a gas-producer to be workable, and its ash content is usually high, limiting its use for coking. If left in the mine as practically useless, it is a source of danger. A recent development in firing with coal-dust is the Bettington boiler.[69] In this appliance small coal and air together pass through a pulverizer, which also acts as a fan, into a separating chamber, through a sieve fixed across the chamber, into a tube which terminates as a vertical water-cooled burner nozzle at the bottom of the combustion chamber. The boiler

[66] *J. Gas Lighting*, 1915, **130**, 93.
[67] U.S. Bureau Mines Tech. Paper 63; *J.*, 1915, 17.
[68] *Engineering*, 1915, **1**, 47.
[69] King, *Priv. Commn.*

consists essentially of a ring of vertical tubes terminating above in a water drum and below in an annular metal chamber; the flame from the mixture of coal-dust and air fills the combustion chamber so formed and the temperature is high enough to fuse the ash, which drops as pellets or trickles down the fire-brick tiles lining the combustion chambers. Care is necessary in choosing the fuel, supplying it reasonably dry, and working the boiler to prevent dust from leaving the chimney top in a partially burned condition; a dust catcher may be usefully installed. The fused clinker drawn from the boiler is thoroughly burned.

The author of the section would like to acknowledge his indebtedness to Messrs. Hodsman and King and the authors of private communications for their valuable co-operation.

GAS—DESTRUCTIVE DISTILLATION. TAR PRODUCTS.

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Carbonization of Coal.

Composition of Coal.

With the object of ascertaining the composition and nature of coal, several investigators have studied the action of different solvents on the coal substance. Pyridine, phenol, and chloroform are the solvents generally chosen, but it is suspected that pyridine may not be an inert solvent, and its use is therefore open to question, there being an increase in the nitrogen content in both extract and residue.[1] The work of Jones and Wheeler,[2] directed towards carefully distilling *in vacuo* the extracts made from coal by pyridine and chloroform, is of conspicuous interest, but at the present stage of the enquiry it is difficult to draw conclusions of technical value. This subject is referred to more fully on page 7.

Thermal Decomposition of Hydrocarbons.

Experiments which have direct bearing on the carbonization process have been carried out by Jones and by Cobb and his pupils. Jones[3] has studied the thermal decomposition of certain hydrogenated aromatic hydrocarbons in contact with porous porcelain. Hexane, cyclopentane, and cycloheptane lose scarcely any hydrogen, whilst cyclohexane and methylcyclohexane yield gaseous products containing 40 % of hydrogen, and the gas from the decomposition of di- and tetrahydronaphthalene contains as much as 80 % of hydrogen. The decomposition of

[1] Parr and Hadley, Illinois Univ. Exp. Stat., Bull. 76; *J.*, 1915, 213.
[2] *J. Chem. Soc.*, **107**, 1318; *J.*, 1915, 1043.
[3] *Ibid.*, **107**, 1582; *J.*, 1915, 1239.

cyclohexanes and tetrahydronaphthalene commences at 490°–510° C., the products of decomposition being in the case of cyclohexane, benzene, hydrogen, methane, ethane, ethylene, and traces of acetylene, and in the case of tetrahydronaphthalene, hydrogen and methane only.

Hollings and Cobb[4,5] report on the subject of the thermal phenomena attending carbonization, and it is most desirable that work of this nature be continued. Various samples of coal were heated under similar conditions to an inert material and the temperature changes observed. In all cases distillation commenced at 250° C., and up to 1100° C.; although various exothermic and endothermic stages of the distillation were observed, the total quantity of heat evolved and absorbed over the whole period was very small. The production of methane appears to be the main exothermic change during the carbonization process, and this occurs notably between 600°–800° C. At lower temperatures (400°–600° C.) oils, unsaturated hydrocarbons, higher paraffins, and oxygenated compounds are evolved; whilst at higher temperatures, above 800° C., the process is thermally neutral or slightly endothermic, the main product being hydrogen. Parallel studies were made with cellulose, dehydrated cellulose, and lignite. The communications referred to not only contain valuable information, but are so suggestive in character that a continuation of this work is most desirable. This remark also applies to the work of the same investigators on the influence of red-hot coke on the gaseous products of carbonization,[6] a question of vital importance to engineers who have to determine the design of retort settings and the method of heating the coal charge. In this work mixtures of gases were heated in contact with coke, the duration of heating in all cases being comparable with the period during which gases are heated in the gas retort. It is pointed out that previous work on the decomposition of hydrocarbons by heat has been applied to the pure hydrocarbons, but the results of this work have no direct bearing on the technical carbonization process, as the questions of the effect of secondary interactions and of the dilution of any particular hydrocarbon by other products of carbonization are determined only by direct experiment. A mixture of equal volumes of hydrogen and methane was accepted as a standard synthetic coal gas, and when such a mixture was passed over heated coke in the standard apparatus used by the authors, only 2 % of the methane was decomposed at 800° C., whilst 65 % was decomposed at 1100° C. To

[4] *J. Gas Lighting*, 1914, **126**, 917; *J.*, 1914, 685.
[5] *J. Chem. Soc.*, **107**, 1106 *seq.*; *J.*, 1915, 862.
[6] *J. Gas Lighting*, 1914, **126**, 924.

this standard mixture, hydrocarbons such as ethane, ethylene, and benzene were added, to the extent of 5 %–10 % by volume, and the degree of decomposition at 800° and 1100° C. was ascertained:—

Hydrocarbon.	At 800° C.		At 1100° C.	
—	Percentage of hydrocarbon decomposed.	Time in seconds.	Percentage of hydrocarbon decomposed.	Time in seconds.
Methane	2 %	57	65 %	46
Ethane	79 %	46	88 %	46
Ethylene	62 %	45	100 %	35
Benzene	nil	51	100 %	42

The work is being continued for toluene and other substances, concerning the stability of which, under the conditions of carbonizing, little is definitely known—surprisingly little considering the obvious desirability for such data. It is generally understood that the gases evolved during carbonization should be removed from the retort as quickly as possible, and the above observations emphasize the necessity of such procedure, as both ethane and ethylene are appreciably decomposed at 800° C.

Distribution of Nitrogen.

Experiments have been carried out by O. Simmersbach[7] to determine the manner in which the nitrogen of the coal becomes distributed between coke, tar, ammonia, hydrogen cyanide, and free nitrogen in the gas at varying temperatures of distillation.

The following table summarizes these results, in which it is shown that the temperature at which the formation of ammonia is at a maximum is about 900° C. In the case of hydrogen cyanide the maximum apparently is not attained at 1200° C.

[7] *Stahl und Eisen*, 1914, **34**, 1153–59 and 1209–13; *J.*, 1914, 781; 1915, 895.

Temperature of carbonization, ° C.	Nitrogen in ammonia. %	Nitrogen in cyanogen. %	Nitrogen in tar. %	Free nitrogen in gas. %	Nitrogen in coke. %
Silesian coal with 6·63 % of ash and 1·396 % of nitrogen.					
600	7·81	0·25	2·12	18·13	71·69
700	18·13	0·66	3·65	12·13	65·43
800	21·28	0·87	3·47	10·73	63·65
850	23·68	1·11	3·72	10·37	61·12
900	24·12	1·19	4·15	12·14	58·40
1000	23·15	1·23	4·11	21·53	49·98
1100	23·09	1·31	3·70	30·51	41·39
1200	22·84	1·42	4·21	45·10	26·43
Westphalian coal with 5·7 % of ash and 1·391 % of nitrogen.					
800	19·46	0·76	1·92	5·88	71·98
850	22·14	1·10	1·77	4·93	70·06
900	19·94	1·11	1·61	9·99	67·35
1000	19·61	1·25	1·87	21·54	55·73

It is known that the decomposition of pure ammonia gas commences at 750° C., and is rapid at 800° C., but experiments have demonstrated that, during the carbonization of coal, the decomposition of ammonia at 900° C. is inappreciable, owing to the high degree of dilution of the ammonia. Similarly, when pure ammonia is conducted over heated coke, the maximum yield of hydrogen cyanide is attained at 900° C., but during the process of carbonization only 5 % of the ammonia is generally converted into hydrogen cyanide. The degree of subdivision of the coal has little effect on the yield of ammonia or on the temperature at which the maximum yield is attained, but the presence of water vapour enhances the production of ammonia.

There is evidence to show that nitrogen exists in coal combined in two or more essentially different ways.[8] For the determination of the nitrogen content the Kjeldahl method gives with some coals only a mere trace, whilst the Dumas method shows about 2 %. As in other cases the two methods are known to give similar results, it is concluded that nitrogen is not similarly combined in all coals. This observation is of importance to investigators endeavouring to augment the yield of ammonia from fuel.

[8] Harger, *J.*, 1914, 391.

Large Scale Carbonization of Coal.

The progress of carbonization on the large scale during the last decade has been definite, but the present position is complicated by the fact that the introduction of the vertical retort has given an impetus to the improvement of working conditions in the older horizontal retort, and both systems consequently claim adherents. Many of the contributions to the subject of coal carbonization may therefore be reduced to a discussion of the relative merits of the two systems. The design of the vertical retort is sound in principle, and aims at subjecting a mass of coal to gradually increasing degrees of heat. In the earlier designs of settings a combustion chamber for the producer gas surrounded the base of the retort, which was therefore subjected to the maximum heat, whilst the products of combustion passed upwards to the top of the setting. It has been assumed that the gases evolved from the coal adjacent to the heated walls of the retort pass upwards to their exit through the central core of uncarbonized coal, and being subjected to gradually decreasing degrees of heat, carbonization under these conditions has been considered to be conducive to the preservation of rich hydrocarbons. On the other hand, Colman[9] states that gas produced in vertical retorts shows evidence of having been exposed to high temperatures, the proportion of hydrogen to methane being even greater than is obtained from the same coal distilled in highly heated horizontal retorts. The tar produced, though containing more paraffinoid constituents than that obtained by horizontal retorts, consists mainly of aromatic derivatives, showing clearly that the vapours produced at low temperatures must have been subjected to a considerably higher temperature before their exit from the retort. It is found that the quantity of sulphur compounds other than sulphuretted hydrogen and the naphthalene content are lower in the gas produced from vertical retorts. Perhaps the chief advantage of such installations lies in the economy of labour charges which results from the facilities afforded for charging the coal and discharging the hot coke. Devices to effect these mechanical operations form the subject matter of recent specifications of the Woodall-Duckham[10] and Glover-West[11] systems of vertical retorts. It is stated that the reduction of labour charges outweighs the increased cost of the vertical retort installation, which, however, requires a smaller ground space than that of the horizontal retort.

[9] *J.*, 1914, 399.
[10] *J.*, 1915, 215 and 860.
[11] *J.*, 1914 910.

As a result of the successful introduction of the vertical retort, the method of operating horizontal retorts has been modified. Not only have substantial improvements been made in the design of the charging and discharging machinery, but the weight of the coal charge introduced into each retort has been materially increased. The use of heavier charges results in a large increase in the volume of gas produced per unit weight of coal, the gas being slightly improved in illuminating and calorific powers. By this means a more cautious distillation of the coal is effected as the heavier charges are raised to the maximum heat of carbonization over a greater time period; and not only has the total illuminating value and calorific value of the gas produced per ton of coal been greater, but the operating difficulties caused by the presence of free carbon in the tar have also been reduced.

The progress in gas works due to the accepted higher standard of manufacturing efficiency is confirmed by the Board of Trade returns. In 1913 the average make of gas per ton of coal carbonized in London was 12,400 cubic feet. In certain isolated cases a yield of 14,000 cubic feet per ton of coal is reported, but such abnormal results should be accompanied by an analysis of the gas, or at least a determination of the inert constituents.

The decision of the works engineer who is confronted with the necessity of selecting carbonizing plant is governed largely by local conditions. Since the outbreak of war the erection of new plant has naturally been restricted. Neill,[12] however, describes a recent installation of Woodall-Duckham vertical retorts at Bolton, and Dickson[13] contributes an interesting paper on the working experience gained with Wilson-Glasgow vertical retorts at Johnstone, N.B. These retorts are specially designed to deal with the secondary coking coals of Scotland.

Waste Heat of Retort Settings.

Concerning the heat balance during coal carbonization, Barnum,[14] as a result of the renewed interest given to the subject by the work of Cobb, has again brought forward the following practical results obtained from a regenerative setting with outside producers :—

[12] *J. Gas Lighting*, 1914, **128**, 302.
[13] *Ibid.*, 1914, **127**, 615; *J.*, 1914, 951.
[14] *Ibid.*, 1914, **127**, 111.

HEAT BALANCE SHEET PER 100 LB. OF COAL CARBONIZED.

—	B.Th.U.	Per cent.
Expended 15·3 lb. coke	195,519	82·6
Heat of formation, plus	40,539	17·4
	236,058	100·0
Accounted for—		
Carried up the chimney	41,165	17·3
In ashes	134	0·06
Carried by gas	14,586	6·0
Carried in tar	4,230	1·7
Carried by hygroscopic water	3,759	1·5
Carried in water formed	8,979	3·7
Loss by radiation and convection	82,643	35·0
In the hot coke	33,396	14·1
Heat of formation, minus	3,966	1·7
Balance (gross heat of carbonization) ...	44,779	18·9
		100·0

Other figures are contributed by Marwick,[15] who assumes that the carbonization of one pound of coal involves an expenditure of 462 B.Th.U., and that the heat unrecovered in gases and vapours is 324 B.Th.U. and the loss in the hot coke (with horizontal retorts) 442 B.Th.U. A total of 1228 B.Th.U. is therefore expended under these conditions, which corresponds to 8·6 lb. of carbon per 100 lb. of coal carbonized. With regenerative settings, the actual fuel consumption is about 16 lb. per 100 lb. of coal distilled. MacLeod[16] gives a corresponding figure of 15·34 lb. of fuel per 100 lb. of coal treated in vertical retorts at Dawsholm.

The gas engineer is from time to time reproached by technical members of other industries for wasting large quantities of heat in various directions in gas works, and several partly successful attempts have been made, especially in Germany, to utilize the surplus heat of retort settings for the production of steam. Schmied[17] renews the question and accumulates figures to show that, by utilizing the sensible heat lost in flue gases and about 50 % of the heat radiated from the settings, the whole of the low pressure steam ordinarily required on the works may

[15] *J. Gas Lighting*, 1914, **125**, 438. [16] *Ibid.*, **127**, 621.
[17] *Ibid.*, **131**, 286.

be generated. To recover the radiant heat, this author is proceeding with experimental trials in which the sides and top of the retort settings are surrounded by a system of water tubes.

Coal with Lime or Limestone admixed.

Of recent years the admixture of lime or ground limestone with coal prior to carbonization has been advocated. Useful work has been carried out by Patterson, who confirms the statement that the volatile sulphur compounds other than sulphuretted hydrogen are reduced by the use of lime so admixed, whilst the yield of ammonia is appreciably increased. All this is compatible with theoretical conceptions, but the experiments quoted from other sources, especially upon the effect of ground limestone, which is stated to enhance the production of liquid aromatic hydrocarbons, are unsystematic, and the results cannot be accepted as conclusive. For several years Vignon has studied the effect of conducting a mixture of water gas and steam over heated lime, whereby methane is produced, the proportion of carbon monoxide being reduced, and that of hydrogen inceased. The following equation is considered to represent the interaction :—

$$2CaO + 3C + 4H_2O = 2CaO + 2CO_2 + 2H_2 + CH_4$$

This investigator[18] has attempted to devise a scheme for the complete gasification of the carbon of coal so as to produce a combustible gas with a low percentage of carbon monoxide. In this process lime is added to the coal, and the whole distilled at 900°–950°C., whereby a yield of about 12,000 cubic feet per ton of coal is attained. Water vapour is then passed over the coke and lime, which increases the yield of gas to about 72,000 cubic feet per ton of coal treated.

The mixed gas has an approximate composition of :—

Hydrogen	70–78 %
Methane	15–20 %
Carbon monoxide	5–10 %

The calorific value is only slightly inferior to that of coal gas. It is stated that practically the whole of the nitrogen of the coal is converted into ammonia.

This process in particular and the effect of lime generally are at present undergoing examination in this country.

[18] *J.*, 1914, 737.

Low Temperature Distillation.

The important question of the low temperature distillation of coal, though frequently referred to and advocated by fuel economists, can only, unfortunately, be cursorily reviewed. Various installations have been operated, but the results obtained are peculiar to each set of experimental conditions. In each case, the varying factors are so numerous—namely, the class of coal, type of retort, the temperature of distillation and the degree of vacuum, if any—that it is impossible to formulate any definite conclusion. The objects of low temperature carbonization are to extract valuable products from the coal prior to its use as a heating agent, and so to limit the extent of the distillation that the residual soft coke may yield the maximum heating effect compatible with the absence of smoke. The products are a light tar, ammonia, and a rich gas. It is generally found that one ton of coal carbonized at about 500°–600° C. yields about 5000–6000 cubic feet of rich gas (which is frequently used for fuel in the retort setting), 18 to 22 gallons of a light tar, which on distillation yields a suitable motor spirit and Diesel and lubricating oils, and ammonia equivalent to at most about 20–25 lb. of sulphate of ammonia.

Probably in no other department of the industry is research so much required as upon this question of distillation at low temperatures, and an investigation of this nature would profit by the experience of the gas engineer and chemist. A perusal of recent gas literature creates an impression that the proposition is generally received with antipathy. This attitude may have arisen as a result of the failure of earlier attempts promoted too exclusively by the financier. The fact remains, however, that raw coal should be treated, prior to its use for industrial and domestic purposes, for the extraction of valuable carbonaceous compounds, ammonia, and sulphur. The richer hydrocarbons produced during the combustion of coal which are recovered by this process, cannot, in most cases, be adequately utilized in existing appliances, and disappear as smoke. The adoption of such a process may solve the problem of the shortage of ammonia in the United Kingdom. An investigation of this nature is one which gas engineers and chemists are eminently competent to undertake, and, moreover, the interests of gas undertakings as purveyors of gaseous fuel need not be affected by the additional responsibility of preparing solid fuel; in fact, in the combination of the two processes appears to lie the ultimate scientific solution of the problem.

Tar Removal and Toluol Extraction.

Fractional Collection of Tar.

Purves,[19] in dealing with the question of the collection of coal tar in fractions, describes a process which consists essentially of consecutively subjecting the gas to different scrubbing systems with anthracene oil, and finally with ammoniacal liquor, whilst the gas is progressively cooled between each scrubbing operation. Cooling is in part effected by air, but as far as possible by an externally applied counter-current flow of tar derived from other carbonizing installations. This tar, after its exit from the heat exchanger, is brought into direct contact with gas in the foul main, so that it is distilled by means of the sensible heat of the crude gas. This author points out that during the ordinary distillation of tar, certain vapour losses ensue, which by this process would be prevented and would augment the volume of permanent gas produced. It is further stated that tar undergoes decomposition on distillation, as the percentage of free carbon is increased. The process is considered to be specially applicable to vertical retort installations, as the low candle power of the gas manufactured arises from the tar fog, which persists in the gas until the final stages of cooling, and when removed carries away the illuminating hydrocarbons.

Electrical Separation of Tar.

The electrical separation of tar from gas has been described by White and others[20] and by Steere.[21] Steere submits gas at a temperature of 65°–80° C. to an alternating high tension discharge of 40,000–80,000 volts, whereby the tar fog is condensed, and may be readily removed by a centrifugal or a Pelouze and Audouin extractor. White, on the other hand, applies electrical separation after the tar extractor, and states that white ammonium sulphate may be obtained from the gas whilst oxide purification is simplified, owing to the absence of tar.

Toluol Extraction.

As a result of the European War, it became necessary to augment the supplies of toluol originating from coal tar, and processes for the extraction of this hydrocarbon from gas have been introduced. Most of the larger gas undertakings erected plant similar in principle to that of the coke oven benzol recovery process, whilst the smaller works (from which the total output of gas is considerable) adopted a simplified method of

[19] *J.*, 1915, 329.
[20] *J.*, 1914, 1000.
[21] *J.*, 1914, 1145; 1915, 415.

toluol recovery known as the "C" process, descriptions of which were privately circulated. The appended references[22] [23] [24] [25] relate to the description of toluol recovery plants, and to the working results to be anticipated. It is inopportune at the present time to discuss this matter in any detail, and the literature on the subject is naturally incomplete, and is in no way representative of the valuable work that has been accomplished.

Ammonia and Cyanogen.

Loss of Ammonia in Storage.

Curphey[26] has determined the loss of ammonia from ammoniacal liquor during storage. Experiments were carried out at five works, and the results show conclusively that a thin layer of oil is effective in reducing oxidation changes and loss of volatile ammonia throughout prolonged periods of exposure. In the case of the storage of 1000 gallons of liquor at 14°–23° C. in a rectangular tank, with one inch air space between the roof and sides, a loss of 43·2 % of the free ammonia was experienced in 80 days. Over a similar period the loss was only 0·5 % from liquor stored under a layer of oil $1\frac{1}{4}''$ thick. Several sets of results are given in the original contribution, and that quoted above is representative of others. Curphey, from actual experience as Chief Inspector of Alkali Works, regards this matter as one of importance, and emphasizes the need of safeguarding against loss. It is further pointed out that this possible source of loss should not be overlooked when comparing the direct with the ordinary method of sulphate of ammonia manufacture.

Ammonium Chloride.

In view of the introduction of synthetic nitrogen compounds on the market in competition with the older sources of supply, Strommenger [27] [28] recommends the production of ammonium chloride from gas-works liquor. The process described consists essentially of treating the liquor, which always contains some ammonium chloride, with a slight excess of hydrochloric acid, the decomposition of other ammonium salts and the oxidation of any iron that is present being facilitated by the passage of a current of air. The liquor is finally freed

[22] Davidson, *J.*, 1915, 170; *J. Gas Lighting*, **129**, 378.
[23] Beckton Process, *J.*, 1915, 416. [24] Diamond, *J.*, 1915, 539.
[25] Herring, *J.*, 1915, 1001.
[26] *J. Gas Lighting*, 1915, **132**, 424; *J.*, 1915, 1247.
[27] *Z. angew. Chem.*, 1914, **27**, 518–20; *J.*, 1915, 17.
[28] *Gas World*, **62**, 446.

from iron by precipitation with ammonia and filtration. The filtrate is neutralized with hydrochloric acid, treated with sufficient common salt to convert the undecomposed sulphate to chloride, evaporated to dryness, and finally the ammonium chloride is sublimed. It is stated that the sublimed salt represents 90–95 % of the original material, and may be dark in colour. In this case recrystallization yields a 100 % salt of permanent snow-white colour.

Liquor Ammonia and Ammonium Sulphate.

The manufacture of liquor ammonia (24·5 % NH_3) is described by Hilgenstock[29] and by Muir.[30] As regards the manufacture of sulphate of ammonia, difficulties arise in working the direct process which are not experienced in operating the old indirect method. It is necessary to maintain strict control over the temperature, density, and free acid content of the saturator, whilst the temperature of the gas also plays an important rôle. The conditions required to maintain regular working are described.[31] An interesting communication has been published[32] on the cause of the discoloration of sulphate of ammonia. The grey coloration is considered to be due to copper and lead sulphides (which originate from the acid used) and to naphthalene contained in the gas. It is generally supposed that the objectionable blue discoloration arises from local alkalinity in the saturator—in fact, Bailey[33] states that this causes a precipitation of iron sulphide, which, with the cyanide compounds contained in the liquor, produces ammonium ferrocyanide and thence Prussian blue. On the other hand, it is considered[32] that Prussian blue originates from the interaction of cyanides and the iron of the ammonia delivery pipe, as well as with that contained in the sulphuric acid. The red coloration is due to iron thiocyanate.

An inspection of the samples of sulphate of ammonia circulated by the Badische Anilin und Soda Fabrik, and produced by the Haber synthetic ammonia process, points to the necessity of improving the average quality of sulphate manufactured by gas undertakings. In a well-arranged plant it is quite practicable to produce a high yield of a good grey salt of the following analysis :—

Ammonia	25·33 %
Moisture	0·25 %
Free acid	0·25 %

[29] *J. Gas Lighting*, 1915, **132**, 436; *J.*, 1915, 1247. [30] *Ibid.*, **129**, 756.
[31] *Gas World* (Coking Section), **62**, March 6th, p. 12; April 3rd, p. 14.
[32] *Ibid.* (Coking Section), **62**, May 1st, p. 18.
[33] *Ibid.* (Coking Section), **62**, Jan. 2nd, p. 13.

Although this material falls below the standard of purity attained by the sulphate from synthetic ammonia, it is distinctly superior to the average quality of sulphate derived from the distillation of coal. The Sulphate of Ammonia Association is fully acquainted with the *status quo*, and has instituted a movement to raise the standard of purity of sulphate of ammonia. Practical recommendations to manufacturers have already been circulated,[34] and it is hoped that this is preliminary to a standardization of working efficiency.

Cyanogen Compounds.

The presence of hydrogen cyanide in the gas is an important factor in retarding the efficiency of oxide purification, as both ferrocyanides and sulphocyanides are produced within the oxide purifier. In the absence of lime purification, cyanogen compounds pass forward to the gasholder and thence to a small extent to the distributing system. The injurious effect of this constituent of gas upon all metals is demonstrated by the facts that metallic cyanide compounds have been detected about the slide valves of dry gas meters, and may be estimated as constituents of the metallic dust found in service pipes. The technical production of potassium or sodium ferrocyanides, Prussian blue, and sulphocyanides is limited by the demands of the market, but the manufacture of potassium and sodium cyanides offers a wider scope in this respect. The production of cyanides from ferrocyanide or sulphocyanide is, however, a complicated process, and it is generally considered that hydrogen cyanide exists to such a small extent in coal gas, and is accompanied by so many impurities (especially sulphur compounds), that the standard of purity required in the finished product cannot be economically attained. For the purpose of eliminating cyanogen compounds from the gas, and at the same time regulating the market value of sulphocyanides, a process[35] has been worked out of hydrolysing sulphocyanides to ammonia. The process consists essentially of treating the ammonium sulphocyanide solution with sulphuric acid of definite strength and volume, at an elevated temperature. The interaction proceeds according to the equations :—

$$2NH_4SCN + H_2SO_4 = 2HSCN + (NH_4)_2SO_4$$
$$2HSCN + 2H_2O = 2NH_3 + 2COS.$$

The ammonia thus produced combines with the sulphuric acid, which is in large excess, and this strong acid liquor is suitable for use in a

[34] Sulphate of Ammonia Association, Jan., 1915.
[35] Evans and South Metropolitan Gas Co., Eng. Pat. 29047, 1913, *J.*, 1914, 953.

sulphate of ammonia saturator. The evolved carbon oxysulphide is conducted into a Claus kiln, and by its partial combustion sulphur is recovered, which serves as the agent for the extraction of further quantities of hydrogen cyanide from the gas. Klason,[36] who studied the hydrolysis of sulphocyanides in 1887, found that the interaction involves the formation of a copious yellow precipitate consisting of compounds of dithiocarbamic acid. The conditions for obviating the formation of such compounds are described in the foregoing patent specification. By another process[37] ammonium sulphocyanide solutions produced from coal gas are distilled with lime to recover the ammonia, and the resulting calcium sulphocyanide solution evaporated to dryness. The residue is mixed with slaked lime and heated to about 540° C., whereby the nitrogen of the sulphocyanide radicle is converted to ammonia according to the equation :—

$$Ca(SCN)_2 + Ca(OH)_2 + 2H_2O = 2NH_3 + COS + CaCO_3 + CaS.$$

It is stated that for the purpose of preventing the formation of urea the carbon oxysulphide is removed by a layer of lime placed over the mixture in the heating chamber.

Sulphuretted Hydrogen and Sulphur Compounds.

Sulphuretted Hydrogen.

In many gas-works the use of lime as purifying material has been abandoned, and whereas formerly oxide of iron was employed only to remove the sulphuretted hydrogen escaping from the lime vessels, it is now required to serve for the removal of the whole of the sulphuretted hydrogen contained in the gas after wet purification. In this reaction the gas (sulphuretted hydrogen) is absorbed by the moist solid oxide of iron, and thus the degree of division and physical condition of the material play an important part. The degree of hydration and the moisture content of the ferric oxide are also essential factors, consequently, the subject is admirably suited for experimentation.

An important contribution is made by Anderson.[38] Pure sulphuretted hydrogen was passed through (*a*) ferric oxide (96·4 % Fe_2O_3), (*b*) ferric hydroxide (Fe_2O_3 66·5, H_2O 17·4, impurities 16·1 %), and (*c*) precipitated ferric hydroxide. The atomic proportion of sulphur absorbed when the material was saturated (as shown by the presence of

[36] *J. prakt. Chem.*, [2], 35, 400.
[37] Williams, Eng. Pat. 2841, 1914, *J.*, 1915, 282.
[38] *J.*, 1914, 683.

sulphuretted hydrogen in the issuing gas), expressed in atoms of sulphur for each atom of iron, was as follows:—

(*a*) 0·48 and 1·06.
(*b*) 0·85 and 0·97.
(*c*) 0·67.

On using moist sulphuretted hydrogen the efficiency of absorption was slightly diminished. It was shown that an increased absorption of sulphur was effected by greater subdivision of the oxide, and with a decreased velocity of the stream of gas. Dry ferric oxide is as active as the hydroxide, but the activity is destroyed by heating. The composition of the spent oxide was the same whether pure or ammoniacal sulphuretted hydrogen were used. From 15 to 38 % of the sulphur could be extracted with carbon bisulphide, and about 4 % existed as iron disulphide, and the atmospheric oxidation of the spent oxide at ordinary temperature gave free sulphur and only traces of ferrous sulphate. By using purified coal gas, to which had been admixed 0·3 to 1·85 % by volume of sulphuretted hydrogen, the spent material contained a much lower atomic proportion of sulphur (0·56–0·19 sulphur for each atom of iron), the proportion in this case being higher with moist than with dry gas. This author has had experience in gas-works with oxides obtained as by-products in copper ore working and in the manufacture of alum from bauxite. Such material, which should not contain more than 25 % of moisture, will absorb 68–69 % of sulphur when finely divided and used without sawdust. Tar, cyanogen, and ammonia were first removed from the gas, and from 2–4 % of air added at the inlet to the oxide purifiers. Using crude gas containing 0·7 % by volume of sulphuretted hydrogen, 1 ton of the new material was capable of purifying 7,835,850–5,879,170 cubic feet when the velocity of gas was varied from 8–10 mm. per second; the volume purified by revivified material varied from 6,761,480–3,868,980 cubic feet at velocities from 6–7·7 mm. per second.

The work of Curphey[39] [40] and his assistants on oxide purification, though it concerns more particularly the treatment of noxious gases from sulphate of ammonia installations, is of considerable importance. A recent communication[41] deals with the evaluation of oxide of iron as an absorbent for sulphuretted hydrogen, and with the part played by ammonia in the foul gases entering the purifier in preventing the "souring" of oxide. Curphey finds that an oxide prepared by drying at 100° C., and remoistening so as to contain 15–20 % of water, is in

[39] *J.*, 1913, 787. [40] *J.*, 1912, 717. [41] *J.*, 1914, 860.

the best condition for absorbing sulphuretted hydrogen. In revivifying it is advantageous to moisten the oxide with ammonia water before heating to 40°–50° C. in air, and remoistening as required with the same solution. In view of the recent attempts to utilize burnt oxide for purification purposes, it is discouraging to find that ignited oxide, although completely sulphided in time, gives a product which is re-oxidized very slowly.

During the period under review no further outstanding work of general interest has been reported. From time to time contributions have been made on the method of operating purifiers, and that known as the backward rotation system is extensively accepted as the most efficient. The relative values of different oxide of iron materials have also been discussed. Such communications are made as the results of large scale experience, and the task of selecting data that may be generally applicable—except, perhaps, over a very extended period—becomes formidable. This statement may be exemplified by summarizing the main factors that have a direct bearing on the working results obtained :—

The nature and origin of oxide of iron used, and the degree of moisture present.

The number of vessels employed in each gas stream, the system of operating the purifiers, and the resistance or back-pressure that may be permitted on each vessel.

The method of charging the purifiers, the depth and area of oxide in each tier, and the number of tiers in each purifier.

The velocity of the gas through each purifier.

The direction of the gas stream in each purifier, and the possibility of reversing the direction of flow.

The quantity of sulphuretted hydrogen and ammonia in the gas.

The amount of hydrogen cyanide, if any, contained in the gas.

The temperature and moisture content of the gas.

The amount of tar and naphthalene remaining in the gas.

The percentage of admixed air, and the point of admittance of air in the purifying system.

Sulphur Compounds other than Sulphuretted Hydrogen.

Carpenter[42] [43] and Evans[44] have fully described a catalytic process for the removal of sulphur compounds from coal gas. In this process

[42] *J. Gas Lighting*, 1914, **126**, 928 ; *J.*, 1914, 682, 737.

[43] *Société Technique de l'Industrie du Gaz en France*, 1913, 245.

[44] *J.*, 1915, 9.

advantage is taken of the facility with which carbon bisulphide in the presence of the hydrogen of coal gas is decomposed by heat, according to the equation :—

$$CS_2 + 2H_2 = 2H_2S + C.$$

A study was made of catalysts which increased the velocity of the interaction, or rather, that allowed the maximum conversion to take place at the lowest practicable temperature. The advantages of selecting the lowest practicable temperature were, firstly, that the interaction might be conducted in iron containers heated externally, and secondly, that the decomposition of the hydrocarbons of the gas should be avoided as far as possible. Reduced nickel was eventually chosen as being most suitable for the purpose. The largest installation described is capable of purifying 15,000,000 cubic feet per day. The plant consists of five units, each comprising a gas-producer and combustion chamber, two heating chambers containing vertical reaction tubes packed with the catalytic material, and two heat interchangers for preheating the gas to 400° C. The reaction tubes are maintained at 430° C. From 78–80 % of the sulphur compounds are converted into sulphuretted hydrogen, which may be removed by oxide of iron.

After about thirty days' use it is necessary to stop the flow of gas through a set of reaction tubes, and to blow air through them in order to burn off the deposited carbon, which is 50 % in excess of the quantity calculated from the amount of carbon bisulphide decomposed. This excess of carbon probably arises from the decomposition of hydrocarbons in the gas, but the following averages of analytical results are quoted to demonstrate that the quantity so decomposed is negligible, as regards its effect on the intrinsic properties of the gas :—

—	Before treatment.	After treatment.
Illuminating power, candles	14·7	14·7
Calorific power, gross B.Th.U.	590·0	594·4
Sulphur ... ... grains per 100 cub. ft.	35·07	7·52
Naphthalene ... ,, ,, ,, ,, ,,	5·54	4·71
Hydrogen cyanide ... ,, ,, ,, ,, ,,	22·19	18·75
Analysis (per cent. by vol.)—		
CO_2	1·44	1·45
C H_m	3·55	3·63
O_2	0·33	0·06
CO	8·16	8·03
CH_4	26·85	27·26
H_2	54·19	54·25
N_2 ... ... (By difference)	5·48	5·32

The cost of operating the process is about 0·3*d.* per 1000 cubic feet. Although sulphuretted hydrogen is produced in the interaction, it is essential to remove this impurity from the gas before treatment in this process. Experiments show that if the quantity of sulphuretted hydrogen in the gas reaches 100 grns. per 100 cubic feet, carbon oxysulphide may be detected in the gas after treatment. This gas is not so readily removed by iron oxide as sulphuretted hydrogen, because the velocity at which it is decomposed into carbon dioxide and sulphuretted hydrogen, according to the following equation, is not rapid :—

$$COS + H_2O = CO_2 + H_2S.$$

Guillet[45] has described important experiments on the decomposition of carbon bisulphide by oxide of iron at comparatively low temperatures. It is found that at temperatures above 25° C. the ordinary oxide of iron purifying material is capable of removing 25 % of the carbon bisulphide of gas. The interaction proceeds according to the equation :—

$$CS_2 + 2H_2O = CO_2 + 2H_2S,$$

the sulphuretted hydrogen being absorbed by the oxide of iron as it is produced. At 100° C. the velocity of the reaction became interesting, whilst at a temperature of 130° C. more than 67 per cent. of the carbon bisulphide originally present in the gas was converted to sulphuretted hydrogen.

Naphthalene.

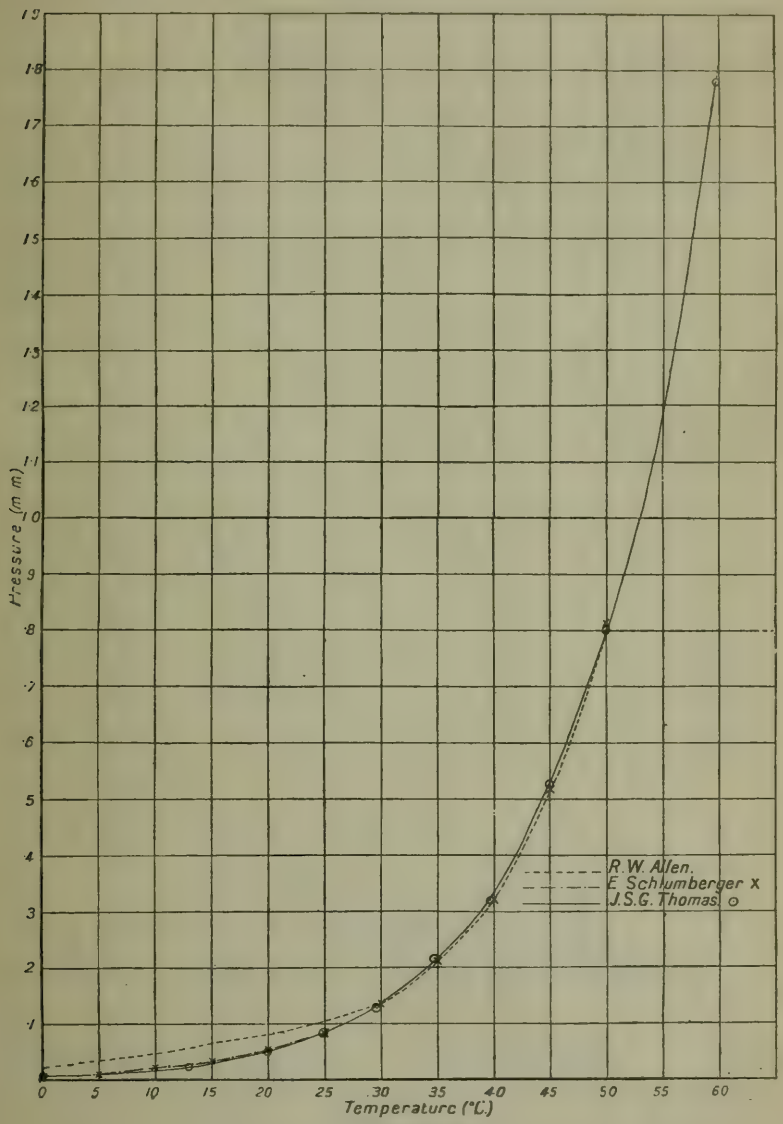
The quantity of naphthalene present in the gas and tar produced with inclined and horizontal retorts is larger than that found in the products from vertical retorts or chamber ovens. A committee of the American Gas Institute[46] has conducted an enquiry into the naphthalene problem, and has found that water-gas tar is generally used for extracting the naphthalene from gas, the quantity used varying from 50 to 250 gallons per 1,000,000 cubic feet of gas treated. Water-gas tar itself is liable to contain much naphthalene if the superheater has been operated above 750° C. Stoppages are frequently cleared by the use of steam and gasoline, but a copious stream of boiling water or a heavy oil is considered to be preferable.

When coal gas is distributed alone, and is not enriched, a cooling plant located at the outlet of the works is suggested, in order to prevent the crystallization of naphthalene following upon the condensation of water from the gas, and to avoid further cooling of the gas in the distributing system.

[45] *Société Technique de l'Industrie du Gaz en France*, 1912, 245.
[46] *J.*, 1914, 66.

Thomas[47] has pointed out discrepancies between the results obtained by Allen and Schlumberger in determining the vapour pressure of naphthalene in coal gas. Allen's value at 0° C. is practically identical

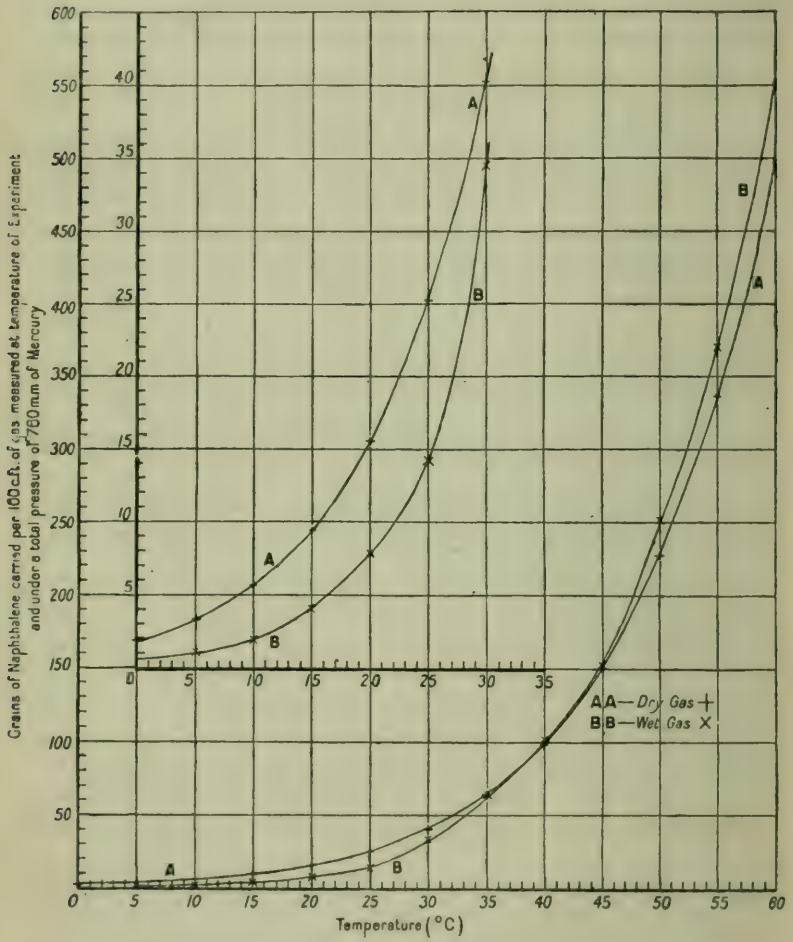
FIG. 1.



[47] *J.*, 1916, 506.

with that found by Schlumberger at 10° C. - a matter of considerable importance to those concerned with the distribution of gas. Thomas has carried out a careful investigation of the vapour pressure of naphthalene, and the results obtained are in substantial agreement with

FIG. 2.


Grains of Naphthalene carried per 100 c.ft. of gas measured at temperature of Experiment and under a total pressure of 760 mm of Mercury
Temperature (°C)
A A—Dry Gas +
B B—Wet Gas X
A
B

those of Schlumberger, but differ from those obtained by Allen for temperatures below 30° C. Determinations have been made on both dry and moist gas. The values obtained by using coal gas are in agreement with those found when the naphthalene is evaporated into

air. The curve shown in Fig. 1 is reproduced to show the values determined by Allen, Schlumberger, and Thomas.

Fig. 2 is a reproduction of a curve by Thomas showing the number of grains of naphthalene carried per 100 cubic feet of dry and moist gas measured at the temperature of the experiment, and under a total pressure of 760 mm. of mercury. In Fig. 2 the inner curve represents the first part of the large curve, and is plotted so that the saturation volumes may be read accurately between 0° and 30° C.

Thomas emphasizes the fact that this work deals only with the evaporation of naphthalene into coal gas, and is not necessarily applicable to its condensation from gas. This problem of naphthalene condensation, which is of even greater importance, requires separate investigation. During the discussion of the paper it was stated that hitherto reliance had been placed upon the results of Allen, which had led to the conclusion that, if the gas contained not more than 10 grs. of naphthalene per 100 cubic feet, no trouble would arise in the distribution system, but although the actual quantity had been maintained below this figure, the trouble had not diminished. In view of the present work it was considered necessary to alter the limit to 2 or 3 grs. per 100 cubic feet in order to be safe.

Tar Distillation and Dehydration.

Apart from the fact that the present time is a most unsuitable one to publish matters dealing with the progress made in tar distillation, the attention of the tar distiller has been devoted to matters of more importance than the preparation of technical communications. Certain analytical methods for the determination of benzene and toluene in coal tar and naphtha have been worked out. Those recommended by Colman,[48] James,[49] and Spielmann and Wheeler[50] appear to be generally applied.

Tar Dehydration.

Chambers[51] has described a plant for the continuous dehydration and partial distillation of coal tar. The Road Board specify three qualities of prepared tar obtained respectively by distillation until the residue has the temperature (1) for road spraying, 230° C. ; (2) for tar macadam, 260° C. ; and (3) for pitch grouting, 288° C. During the "dehydration" of ten tons of crude tar, 300 gallons of light oils are generally produced ; these give on rectification 25 gallons of crude carbolic acid, 25 gallons of cresylic acid, 30 gallons of 90% benzol, 20 gallons of 90% toluol, 40 gallons of solvent naphtha, and 150 gallons of light creosote oils.

[48] *J. Gas Lighting*, 1915, **129**, 314; *J.*, 1915, 217. [49] *J.*, 1916, 236.
[50] *J.*, 1916, 396. [51] *J.*, 1915, 1202.

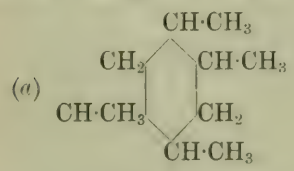
The danger of boiling over is obviated in the installation described by this author by maintaining a shallow layer of tar in the still, and a large vapour space above it. By a counter-current heat-interchanging system the tar is preheated before distillation. A communication by Livesey[52] gives the results obtained by the operation of a Wilton's continuous still. In both cases the financial aspect of the question is analyzed.

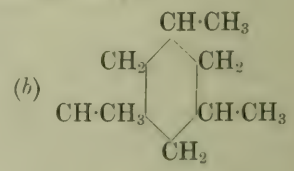
Constitution of "Vacuum" Tar.

An interesting paper by Pictet and Bouvier[53] deals with the saturated hydrocarbons of "vacuum tar." The separation of saturated and unsaturated hydrocarbons was effected by liquid sulphur dioxide. The fractional distillation at atmospheric pressure of the hydrocarbons remaining undissolved yielded four well-defined compounds, which, added to those already isolated, increased to six the number of hydrocarbons now isolated from such tar. The composition of all these corresponds to the general formula C_nH_{2n}, and they form a continuous series and are probably homologues of cyclohexane. The principal properties of these hydrocarbons are specified as follows :—

Hydrocarbon.	Boiling point.	Specific gravity.	Refractive index at the same temperature.
C_9H_{18}	135°–137° C.	0·7590 at 20° C.	1·4212
$C_{10}H_{20}$	160°–161° ,,	0·7680 ,, 20° ,,	1·4272
$C_{10}H_{20}$	172°–174° ,,	0·7765 ,, 23° ,,	1·4196
$C_{11}H_{22}$	189°–191° ,,	0·7838 ,, 22° ,,	1·4234
$C_{12}H_{24}$	211°–213° ,,	0·7862 ,, 21° ,,	1·4293
$C_{13}H_{26}$	227°–229° ,,	0·7953 ,, 20° ,,	1·4379

The hydrocarbon $C_{10}H_{20}$ had previously[54] been identified as hexahydrodurene (*a*) (1. 2. 4. 5-tetramethylcyclohexane). It was possible to determine precisely the constitution of one of these compounds, C_9H_{18}, which may be regarded as hexahydromesitylene (*b*),





[52] *J.*, 1915, 1238.

[53] *Comptes rend.*, **160**, 629; *J.*, 1915, 604.

[54] Pictet and Bouvier, *Comptes rend.*, **157**, 1436; *J.*, 1914, 70.

since dinitromesitylene is produced by its nitration. Above 240° C. it is necessary to distil the tar under reduced pressure in order to prevent decomposition. By extracting such distillate with cold acetone, and repeatedly crystallizing, a saturated hydrocarbon ($C_{30}H_{60}$) was obtained, which is a homologue of the above series. This hydrocarbon exists in coal, from which it may be extracted by boiling benzene, and the author also succeeded in extracting it from Galician petroleum paraffin. It is remarkable that the compound is identical with the melene obtained by Brodie in 1849 by the dry distillation of beeswax.

Isoquinoline.

Isoquinoline, which has a technical value for therapeutic purposes and in the manufacture of perfumes, occurs in coal tar to the extent of about 1 %. To separate it from quinoline, advantage is taken of its greater basicity.[55] The crude quinoline is partially or completely neutralized,[56] and then treated with a quantity of alkali insufficient to liberate the whole of the bases. The more strongly basic fraction is further treated to yield a salt of pure isoquinoline by crystallization of its acid sulphate.

Coke and Coke Ovens.

The Coking Property of Coal.

The property in coal of forming coke appears to depend upon the presence of constituents which melt at a lower temperature than that at which the rate of decomposition or carbonization becomes rapid. Certain of these constituents are readily oxidized, and this property is considered to account for the fact that the coking property of coals is diminished by exposure to air. By heating coal in an inert atmosphere for several hours at 300° C., the coking power of some coals is destroyed and of others weakened.[57] The true coking coals appear to retain sufficient resin-like bodies after being heated to about 300° C. to yield the necessary fusible material to form coke when heated to 320° C. or above. Feebly coking coals yield a similar fusible body, but the quantity is insufficient to melt or render liquid the whole of the material, and coke is not formed.

Investigators are in agreement that the true coking coals in addition to the so-called resin-like bodies (which produce a slight coking effect) contain a class of substances which are not soluble in alkali, do not oxidize in warm air, and do not decompose or volatilize at 300° C., and

[55] Weissgerber, *Ber.*, 1914, **47**, 3175; *J.*, 1915, 651.
[56] Ges. f. Teerverwertung, Ger. Pat. 285666, 1914, *J.*, 1915, 1134.
[57] Harger, *J.*, 1914, 391.

that substances of this class melt when strongly heated, yielding enough luting or cementing material to form coke.

Cooper[58] states that coal containing more than 8 % of oxygen on an ash and moisture free basis has generally poor coking properties. This author finds that the behaviour of the dried coal on distillation is a criterion by which to judge of its power to form coke, and submits a series of results which are given in the following table. It is concluded that if the yield of water from the dry coal exceeds 7–8 %, the coke produced will be inferior.

Coal.	Coke. %	H_2O. %	CO_2. %	CO. %	Remarks.
Cumberland	69·8	5·34	0·94	6·0	Good coke
Durham	76·5	4·11	1·02	4·6	,, ,,
Warwick	62·0	12·98	3·60	10·6	Poor ,,
Monmouth	80·0	3·37	0·51	3·2	Good ,,
Staffordshire	71·0	7·53	1·08	4·9	,, ,,
Yorkshire	70·0	6·66	1·28	7·8	,, ,,
Lancashire	70·0	6·80	1·48	5·2	,, ,,
Lanark	65·0	8·09	2·45	10·7	Fair ,,
Fife	68·0	9·12	1·99	7·6	Good ,,
Northumberland	67·0	8·55	2·46	7·8	Fair ,,
Forest of Dean	68·0	6·73	1·58	7·5	,, ,,
Brown coal (Australia) ...	48·0	12·78	8·22	23·0	Poor ,,
Leicester	63·0	10·52	2·74	12·4	,, ,,
Lancashire Cannel... ...	63·0	6·19	0·56	5·6	,, ,,

Coke Ovens.

Considerable progress has been made recently in rendering the operation of coke ovens more efficient, and greater attention has been devoted to the effective recovery of by-products. As regards the yield of coke, Purves,[59] operating with an Otto direct ammonia recovery plant, obtained 78·75 % by weight of the dry coal, the nature of the coke being as follows:—Large coke, 94·14 %; nuts, 3·19 %; breeze, 2·67 %. It contained about 1 % of moisture, and the selling price was 7*s.* 0·4*d.* per ton above that realized by the gas-works coke at Glasgow. The yield of sulphate of ammonia varied from 33 to 39 lb. per ton of dry coal treated. By ensuring thorough carbonizing towards the end of the heating period, the yield of gas was materially increased.

[58] *J. Gas Lighting*, 1914, **127**, 722. [59] *Ibid.*, **126**, 948.

Coke oven gas is supplied for town lighting in Middlesbrough[60] from the Newport Iron Works. The average calorific value of the gas is 600 B.Th.U. per cubic foot, but variations occur when gas from a newly charged oven is distributed. The required quality of gas is obtained by providing a separate main for the rich gas produced in the early stages of carbonization, whilst the poor gas given off later on is employed for heating the ovens. Experience shows that the yield of rich gas of 620 B.Th.U. per cubic foot is about 5800 cubic feet per ton of coal carbonized, and that of poor gas of 490 B.Th.U. per cubic foot is about 4450 cubic feet. Thus, although the gas used for heating the ovens represents from 50 to 60 % by volume of that produced, the actual expenditure when reduced to a heating value basis is only 38 % of the total production. The above figures refer to coke ovens of the regenerative type, as those designed on the "waste heat" principle employ for heating purposes from 70 to 90 % by volume of the gas made. A communication by Witzeck[61] deals with the history and development of the coke oven industry, and contains detailed descriptions of modern installations. The author enumerates the advantages to be realized by manufacturing metallurgical coke on a site adjacent to the coal mine, and by distributing the gas to towns through a long distance transmission system. Simmersbach[62] gives some interesting analyses of the gas made by coke ovens during each of the twenty-nine hours constituting the full carbonizing period. This information, though valuable, is incomplete without the knowledge of the actual quantity of gas produced hourly.

Incandescence Mantle.

Stern[63] communicates interesting figures pertaining to the incandescence mantle industry in which 300 tons of thorium nitrate are consumed per annum, representing about 3300 tons of monazite sand. The cerium oxide recovered annually from this quantity is over 1000 tons, and only 3 tons are actually required for the mantle industry. About 200 tons of cerium oxide are employed for the manufacture of pyrophoric alloys, and 300 tons for impregnating arc-light carbons. A ton of sand, costing £30, contains 2·5 mgrms. of radioactive mesothorium, of which 2 mgrms. (value £30) are recoverable. The demand for this element for therapeutic purposes will perhaps increase, but as the mantle industry cannot absorb more thorium, the extraction of

[60] *J.*, 1915, 70; *J. Gas Lighting*, **128**, 726.
[61] *Journ. f. Gasbeleucht.*, **57**, 361-8, 389-92.
[62] *J. Gas Lighting*, 1914, **127**, 465.
[63] *Z. angew. Chem.*, 1913, **26**, 806; *J.*, 1914, 69.

larger quantities of mesothorium depends upon the profitable utilization of cerium.

It has become the practice to recover rare earths from mantle dust, and by this means material for the impregnation of 270 mantles is obtained from 1000 used mantles.[64] The ash is digested with strong sulphuric acid at 200° C., precipitation is effected by oxalic acid, and the mixed oxalates are washed, and then dried at 130°–140° C. The nitrates are produced by boiling the oxalates with nitric acid of specific gravity 1·4, and evaporating the solution to dryness. Before use the recovered material may need the addition of cerium nitrate.

In an enclosed space at uniform temperature the Welsbach mantle radiates no more light than other incombustible substances, but within a flame the mantle becomes hotter (and more nearly approaches the temperature of the flame) than any other known substance, owing to the transparency of its substance in the infra-red region. In virtue of this transparency the mantle is unable to give off as heat wave energy the heat imparted to it by the burning gas.[65] The incandescence mantle therefore functions as a heat-light engine. In this respect Rubens[66] has found that a cerite mantle placed in the flame of a Bunsen burner acquires a relatively low temperature of 1350° C., whilst a thorite mantle and Auer mantle under similar conditions attains 1900° and 1800° C. respectively. In experiments made by Bertin[67] water was heated above similar burners, one carrying an Auer mantle and the other a cerite mantle. The temperature of the water above the Auer mantle increased more rapidly than that above the cerite mantle, owing to the greater heat of the products of combustion. If, on the contrary, the flasks of water were placed at the sides of the mantles, the water adjacent to the cerite mantle was more quickly heated, showing that in this case a greater quantity of heat was transferred into radiant energy than in the case of the Auer mantle. Actual radiation measurements were made by thermopile, and the following galvanometer readings were recorded:—

Naked flame	2·5
Auer mantle (Plaissetty)	5·0
Cerite (Delage)	8·5

Delage proposes to take advantage of the superior radiating effect from cerium oxide for general heating purposes, as the use of this oxide should be of considerable industrial and economic importance in presenting an outlet for a portion of the residues after the extraction of

[64] Du Chattel, *J. Gas Lighting*, 1915, **132**, 439.
[65] Haber, *J.*, 1914, 51. [66] *J. Gas Lighting*, **126**, 504. [67] *Ibid.*

thorium from monazite sand. A radiator has therefore been devised consisting of a range of six high-power burners capped with mantles of knitted asbestos impregnated with cerium oxide. Working normally, the yield from this radiator, fitted with the asbestos-cerite mantle, was 91 % higher than that given by the Bunsen flames, and 23·25 % higher than that of the Auer mantle.

Ventilation.

An important investigation into ventilation has been carried out by a Joint Committee representing the Institution of Gas Engineers and the University of Leeds. As far as possible, the experimental room (which is described in the first report[68] of the Committee) conformed to the requirements—firstly, that the air entering should be maintained at a constant temperature and possess a uniform chemical composition, and, secondly, that the air should enter and leave the room steadily, and, as far as possible, through known openings. In the first report the general method of experiments proposed to be followed in the research is discussed, and an ingenious apparatus for comparing the drawing powers of gas burners is described. This consists essentially of a delicately balanced mica vane attached to a small magnet, which serves as the detector of air currents, and when the vane is undeflected, a measurement of the relative areas of the openings into the respective chambers in which the burners are placed enables the drawing powers to be directly compared. In the second report[69] of the Joint Committee details are given of experiments carried out with this apparatus. It is shown that whenever a burner is used in conjunction with a flue for ventilating purposes, there is a position of maximum efficiency at which the burner should be placed relatively to the flue, and the factors determining this position are given. The ventilating powers of various types of burners were directly compared by the use of the apparatus described above. It was found in the case of inverted burners that those allowing a clear passage for the gases into the flue possessed the greatest efficiency, and thus the use of deflectors intended for the protection of fittings from the action of the products of combustion reduced the efficiency. It was further demonstrated that globes with a very open base had no effect on the ventilating efficiency, whilst those with a constricted opening produced a reduction dependent on the area of the opening.

Experiments were carried out to determine the relationship between the volumes of air moved and of gas burnt. It was found that the

[68] Harrison, *J. Gas Lighting*, 1914, **126**, 902; *Trans. Inst. Gas Eng.*, 1914, 123.
[69] Harrison, *Ibid.*, **130**, 573; *ibid.*, 1915, 56.

injector ventilating action of the unlighted moving gas is roughly proportional to the gas consumption, the total volume affected by the injector action being approximately eleven times the volume of gas employed. The gas when ignited produces (in the case of a gas fire) a ventilating effect due to the motion of 400 times its volume.

Chemical and Physical Characteristics of Coal Gas.

Pierce[70] has carried out a series of determinations on the illuminating effect of gas burners using gas of widely varying physical characteristics, and states that the calorific power, candle power, and specific gravity do not adequately define a gas for commercial purposes. The work was carried out with only one upright burner, which was adjusted to yield the maximum effect from each sample of gas under observation, and this probably accounts for the abnormal results obtained. A portion of the contribution deals with the effect of the humidity of the atmosphere on the illuminating power developed, and is of considerable importance. An examination of the results contained in the paper and in many others of a similar nature that are from time to time published emphasizes the need for gas undertakings to distribute a gas of constant physical characteristics and maintained at a uniform pressure. Although it is impossible to maintain these conditions rigidly, considerable progress in this direction has been made during recent years, especially in the case of large gas undertakings. This problem is an exceedingly difficult one for gas-works admixing carburetted water gas to the coal gas manufactured, and this is a hindrance to the adoption of this system. Even in the case of works distributing coal gas only, a considerable variation may occur by inattention to retort-house conditions. In this respect observations made by Newbigging[71] are of interest in showing the effect on the quality of the gas produced by slightly varying the pressure conditions in the retort.

The specific gravity of the gas is no real criterion of constancy,[72] as an increase in the incombustible constituents, nitrogen and carbon dioxide, produces the same effect as an increase in valuable hydrocarbons in elevating the density. On the other hand, the determination of the proportion of nitrogen contained in the gas is of value as indicating the efficiency of retort-house control. Experience shows that the gas, even after the use of 2 % of air for purification, need not contain more than 7 % to 9 % of nitrogen. The extent to which this limit may be overstepped is seen from a statement of Leech[73] that one

[70] *J. Gas Lighting*, 1915, **131**, 192. [71] *Ibid.*, **129**, 509; *J.*, 1915, 267.
[72] Cranfield, *J. Gas Lighting*, 1915, **130**, 139. [73] *Ibid.*, **128**, 555.

Samples of Gas taken from the Foul Main at the Retort-House Governor.

—	Carbon Dioxide.	Oxygen.	Illuminants.	Carbon Monoxide.	Methane.	Hydrogen.	Nitrogen by Difference.	Total Non-Combustibles.	Calorific Value in B.Th.U. per Cub. Ft.	
1	3·50	0·50	5·80	7·50	39·36	38·57	4·77	8·27	677·1	
2	3·50	0·30	5·60	7·30	37·27	36·60	9·43	12·93	644·6	
3	3·40	0·30	4·90	7·40	35·28	40·11	8·61	12·01	620·0	Gauge showing 1/10th pressure.
4	3·40	0·60	4·60	7·80	33·44	41·26	8·90	12·30	599·5	
5	3·60	0·40	4·20	7·80	32·59	42·13	9·28	12·88	584·5	
6	3·50	0·30	4·00	7·80	31·81	44·67	7·92	11·42	580·2	
1	4·70	0·50	3·80	8·10	27·52	38·66	16·72	21·42	513·9	
2	4·20	0·20	3·20	8·00	24·39	39·56	20·45	24·65	471·5	
3	5·00	0·80	3·10	7·00	25·87	36·67	21·56	26·56	471·5	Gauge level.
4	5·30	0·60	2·90	7·60	23·59	39·10	20·91	26·21	453·7	
5	5·30	0·70	2·80	7·40	23·80	36·20	23·80	29·10	443·6	
6	5·30	0·90	2·90	7·30	23·51	35·07	25·02	30·32	439·0	
1	4·20	4·60	2·60	5·70	21·88	27·39	33·63	37·83	385·9	
2	4·40	1·60	3·60	6·10	25·38	33·85	25·07	29·47	466·3	
3	4·80	1·40	3·00	5·70	22·46	33·35	29·29	34·09	420·1	Gauge showing 1/10th vacuum.
4	4·90	2·00	2·90	5·90	20·60	33·09	30·61	35·51	399·0	
5	5·20	2·40	2·60	5·40	19·38	31·44	33·58	38·78	372·9	
6	5·30	2·60	2·40	5·50	17·95	32·03	34·22	39·52	356·1	

The retorts from which the above samples were taken are horizontals worked with a dry main, the main being sealed during the time occupied by drawing and charging. The retorts are charged with a Fiddes-Aldridge machine. The first sample was taken immediately after closing the last mouthpiece lid after charging, the remainder at intervals of about 25 minutes—the last sample being taken just prior to sealing the main in readiness for the next charge.

of the works (now obsolete) of the Leeds Corporation manufactured gas with no less than 39 % of inert constituents. In a former portion of this report it is pointed out that a knowledge of the make of gas per ton of coal carbonized is without value unless the volume is expressed in terms of a standard gas.

Experience has shown that the consumer seldom takes advantage of the fact that most burners are fitted with means for adjusting the supply of air and gas, and that such adjusting screws are liable to be deranged in the most unsuspected of ways.

If, however, gas were distributed of uniform characteristics and maintained at a constant pressure, it would be practicable to supply the gas consumer with appliances standardized to work at maximum efficiency. The use of gas for the production of heat and power falls outside the scope of this sectional report, and reference is made only to an inverted incandescent gas burner[74] designed for gas of approximately constant composition. It possesses no means of regulating the air or gas supply, as none is required.

As regards the question of the degree of purity that should be attained, sulphuretted hydrogen is entirely removed before the distribution of gas to the consumer, and this is also practically the case with the ammonia impurity. Hydrogen cyanide, though yielding no deleterious product on complete combustion, has an injurious effect prior to combustion on metal work which fully warrants its removal. Further, the extraction of hydrogen cyanide and its conversion to ammonia is a sound commercial proposition. The removal of sulphur compounds other than sulphuretted hydrogen has been the subject of much legislation, as shown in a careful review of Clowes.[75] It is to be regretted that, although the sulphur compounds remaining in gas may be reduced to very low figures, no process has yet been devised that will entirely eliminate this impurity. It is the opinion of certain gas engineers that every effort should be made by the chemist to devise means to remove this sulphur entirely, and it is anticipated that work in this direction will be resumed when a moment more opportune than the present is reached.

[74] Carpenter, Eng. Pat. 25874, 1911.

[75] *J.*, 1916, 581.

MINERAL OILS.*

By J. W. Cobb, B.Sc.

Much work has been done for some years past with a view to increasing the production of petrol from crude oil, the demand for petrol having outgrown the supply obtainable by simple distillation. This demand has now become more urgent and has been supplemented by the need for benzol and toluol. Cracking the heavier portions of oil has received considerable attention, and in some form or other has been the subject matter of a number of processes and patents. According to Rittman[1] three methods have been adopted:

(1) Cracking at ordinary pressures.
(2) Cracking under increased pressure in stills.
(3) Cracking under pressure in tubes.

The first method has been found unsatisfactory on account of excessive production of olefines, and the second is dangerous on account of the large volume of oil heated under pressure, but the tube methods are more promising if the difficulty from carbon deposits can be met satisfactorily.

Nevertheless, it is pointed out that the best-known cracking process —the Burton process, used by the Standard Oil Co.—is carried out in a large still under pressure.

The increased demand for the light aromatic hydrocarbons has given rise to a new development of the cracking process in America, and Rittman[1] and collaborators at the Bureau of Mines claim to have successfully produced aromatic hydrocarbons on a large scale from American petroleum. The production of aromatic hydrocarbons from petroleum is by no means new, but the older processes have been directed to the treatment of such petroleum as the Rumanian, rich in cyclic compounds, and favourable to conversion. American petroleum is well known to be almost devoid of cyclic or aromatic constituents.

* *See* Note on page 66.

[1] Rittman, Dutton, and Deane, U.S. Bureau of Mines, Bull. 114; *J.*, 1916, 1003.

Rittman has studied the conditions of cracking American petroleum in great detail, so as to define the conditions favourable to the formation of ordinary petrol, and of aromatic hydrocarbons.

Cracking in this process is effected in a vertical iron tube, and according to the nature of the product desired—benzene, toluene, or petrol—the pressure, rate of feed, and temperatures, are adjusted. Petrol formation is found to be favoured at temperatures from 500° to 575° C., and pressure from 250 to 300 lb. per square inch. Where maximum benzene yield is sought, 600° to 750° C. and 250 lb. per square inch are the approved conditions, with 150 lb. to the square inch for toluene. The cracking of various commercial tar products was also given some attention.

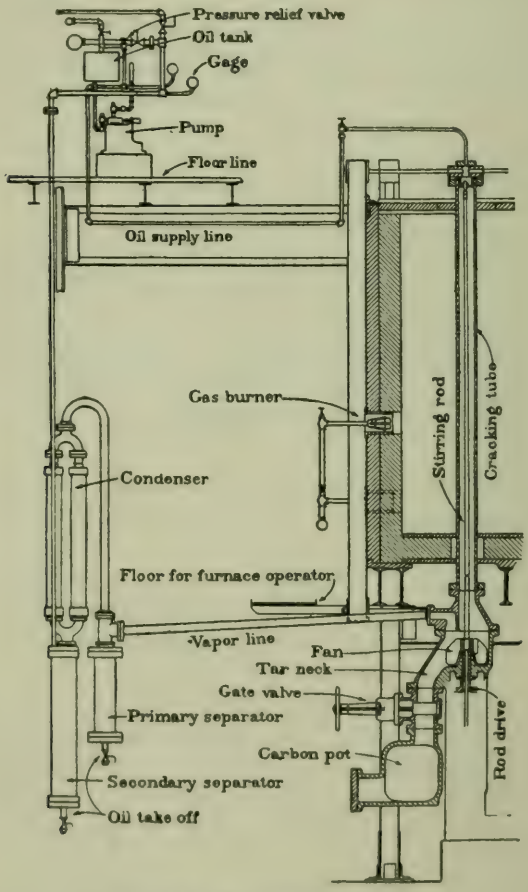


DIAGRAM OF CRACKING PLANT.

The process can be followed from the diagram, in which the parts are clearly shown. The oil to be cracked is forced by a pump into the top of the cracking tube fixed vertically in a gas-heated chamber, the maximum temperature of which is attained in the lower half. The stream of oil is broken up and descends to be vaporized. A considerable pressure is maintained in the tube. Cracking occurs mainly in the lower part of the tube, with the production of tars and of free carbon which accumulates. To prevent choking of the tube with carbon, a stirring rod passes through it, so fitted with small chains that when the rod is revolved the chains are flung out and scrape the walls of the tube. Below the furnace floor cooling commences and tar and pitch separating out are collected in the so-called carbon pot. Vapours pass on to the primary separator, where a separation of heavier oils occurs, then through a water-cooled condenser and into a secondary separator. Gases and vapours still uncondensed go on to a scrubber. The furnace product is thus fractionally condensed, saving preliminary distillation in the rectification of the light oils.

Rittman's general conclusions on the cracking process have been since embodied in the following scheme :—

Heavy petroleum hydrocarbons. ⇄ Light petroleum hyrocarbons saturated and unsaturated.

↓

Cymene.

↓

Xylene.

↓

Toluene.

↓

Benzene.

↓

Naphthalene, diphenyl, etc.

↓

Anthracene, etc.

↓

Carbon and gas.

This is supported by tabulated results. The opinion is expressed that the reactions are not reversible to any appreciable extent.[2]

Rittman's work on the " manufacture of gasoline and benzene-toluene

[2] Rittman and Others, *J.*, 1916, 105, 169.

from petroleum and other hydrocarbons," is described in a paper of 268 pages and much detail is given, but internal evidence is not convincing as to a sufficiently complete chemical examination of products with a view to determining their real composition, as distinguished from their comparative volatility or temperature range of distillation.

A method of cracking petroleum for petrol and aromatic hydrocarbons, which has special features, and has been described in some detail, is that of Hall.[3] The process is of the "tube" type. Oil is fed at 50 to 75 lb. pressure into a system of 300 feet of 1-inch pipe, maintained at 550° C., in such a manner that the vapours travel at 5000 to 6000 feet per minute, whereby the deposition of carbon, formed in the cracking, is stated to be minimised. The vapour then escapes into a larger vessel with a reduction in velocity and pressure, and an increase in temperature. Free carbon is then filtered out by a packing of iron tubing, further cracking occurs, and hydrogenation of unsaturated hydrocarbons. Fractional condensation follows.

The use of catalysts to facilitate the production of the lighter gasoline from the heavier kerosene has been made the subject of experiment by Egloff and Moore.[4] A kerosene (of density 0·800 at 15·5° C.) from Pennsylvania petroleum was used; 400–500 c.c. was heated for three hours, with 10 % of solid catalyst, in an 800 c.c. flask with a still-head, and an inlet for hydrogen and chlorine. The percentages of gasoline produced by catalysis with magnesium, zinc, sodium, and aluminium in presence of hydrochloric acid were 1·0, 4·9, 5·3, and 37·3 % respectively. With magnesium, aluminium, silicon, sulphur, phosphorus, and selenium, in presence of chlorine, the percentages were 0·3, 15·9, 0·6, 0·7, 1·7, and 5·3 % respectively. The figures for aluminium are striking.

Another process which is claimed to produce largely increased yields of light hydrocarbons is that of A. M. McAfee.[5] The oil, after having been freed from water and lighter products, is distilled with anhydrous aluminium chloride in a still provided with a stirrer. Distillation is carried out at about 260°–290° C., and usually occupies from 24 to 48 hours. High-boiling constituents and volatilised aluminium chloride are condensed from the vapours in two air-cooled condensers, connected in series, and are returned to the stills, and the vapours, at a temperature about 175° C., pass finally to a water-cooled condenser. The condensed products are stated to be saturated and to require no sulphuric acid treatment; they are freed from hydrogen sulphide by

[3] *J. Inst. Petrol. Tech.*, 1915, **1**, 147; *J.*, 1916, 296.

[4] Egloff and Moore, *Met. and Chem. Eng.*, 1916, **15**, 67; *J.*, 1916, 882.

[5] *J. Ind. Eng. Chem.*, 1915, **7**, 737–741; *J.*, 1915, 1002.

washing with alkali and water. The yields of gasoline from Caddo and Oklahoma oils are stated to be 43·3 % and 34·8 % respectively, compared with 18 % and 12·5 % by the ordinary cracking process. The aluminium chloride is recovered from the coke residue by treatment with chlorine at red heat.

Rittman, Byron, and Egloff,[6] examined the cracking of aromatic hydrocarbons in the vapour phase at 650°, 725°, and 800° C., finding that decomposition proceeded thus :—

Higher benzene homologues → lower benzene homologues → diphenyl → naphthalene → anthracene.

A. P. Bjerregaard[7] has made some interesting experiments to ascertain the effect of pressure and rate of feed on the yields of low-boiling oils from crude oil. The experiments were carried out in a coil of iron pipe, 63 feet long, with crude oils and with kerosene, at pressures varying from 275 to 1400 lb. per square inch, and temperatures from 340° to 440° C. In all cases the greatest yields of low-boiling oils were obtained when a low rate of feed (3·7 gallons per hour) was maintained, and at this rate the yield was practically independent of the pressure and kind of oil used. When the oil was fed at 12·25 gallons per hour, no products having boiling-points below 220° C. were obtained. The best yields of low-boiling oils (boiling below 220° C.) from crude oils were 40·3 % at a pressure of 275 lb. per square inch and 350° C., and 42·3 % at 1000 lb. per square inch and 395° C., the rate of feed being 3·7 gallons per hour in each case.

Brooks and his co-workers[8] have also examined the effect of pressure on the yield of low-boiling oils. Working with an Oklahoma crude oil, from which the gasoline and kerosene had been removed, they found that the yield of gasoline distilling below 150° C. increased with rise of pressure to a maximum of about 33 % at 280 lb. per square inch pressure, and then slowly diminished.

A considerable amount of interest has been attracted to the work of W. O. Snelling,[9] who has succeeded in producing a more or less definite mixture of hydrocarbons, resembling crude petroleum in appearance and properties, from vaseline, sod wax, gas oil, and similar hydrocarbon materials low in hydrogen. The material was heated in a closed vessel, of which it occupied from one-tenth to one-half the

[6] *J. Ind. Eng. Chem.*, 1915, **7**, 1019–1024; *J.*, 1916, 105.

[7] *J. Ind. Eng. Chem.*, 1915, **7**, 573–577; *J.*, 1915, 824.

[8] B. T. Brooks, R. F. Bacon, F. W. Padgett, and I. W. Humphrey, *J. Ind. Eng. Chem.*, 1915, **7**, 180–185; *J.*, 1915, 412.

[9] *Amer. Inst. Min. Eng.*, Feb., 1915; *J.*, 1915, 267.

space, until a pressure of 800 to 900 lb. was attained. By alternately distilling the "synthetic crude oil" thus produced and reconverting the residue under pressure, from 50 to 70 % of the original hydrocarbon material was obtained as gasoline of sp. gr. about 0·67.

Much work along the same lines, or for the same purpose as that described above, has been done in this, and no doubt in other countries during the war period, but publication has, of necessity, been deferred. In all such work a primary difficulty is not the production of a certain amount of the substance sought, but its production in the pure state or in such favourable admixture that purification, with implied consumption of sulphuric acid, etc., may be economically effected.

NOTE.—The foregoing summary does not claim to be a full treatment of the subject of mineral oils. The notes were originally prepared as part of the section on "Fuel," and deal only with recent work on the "cracking" of mineral oils, in which considerable progress has been made during the period under review.

COLOURING MATTERS AND DYES.

By Gilbert T. Morgan, D.Sc., F.R.S.

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During the period under review in this report several circumstances arising out of the world war have combined to bring into special prominence the manufacture of synthetic colours and their parent substances. So important are these factors that it is already evident that the ensuing changes in the conditions of the colour industry amount to nothing less than the beginning of a new epoch in the development of this branch of applied chemistry.

During the earlier period which, after lasting nearly sixty years, ended in 1914, the manufacture of synthetic dyes had become increasingly a German monopoly. A few enterprises—notably those of the Swiss colour-makers—still continued the industrial struggle against heavy odds, but they were the honourable exceptions to the general rule. The line of least resistance more often followed by reputed dye-makers outside Germany was either to assemble German intermediates and convert them into dyes, or, more lucratively, to purchase finished German dyes, and, after breaking bulk, to purvey them, *cum grano salis*, to dye users at enhanced prices.

The outbreak of war demonstrated to the general public of the allied and neutral nations two cardinal facts which had long been appreciated by chemists having expert knowledge of the coal-tar industries. The first of these facts to attract public attention was the serious hindrance to great industrial undertakings in all civilized countries of the globe by the stoppage of German dyes. The interests affected in Great Britain alone were estimated at an annual value of £200,000,000 sterling. The second fact which became patent as the military exigencies involved an increasingly lavish use of artillery of all calibres was the intimate connection between the production of dyes and the manufacture of high explosives. In Germany the huge plants of the colour factories were easily and swiftly diverted to the making of these essentials. The absence of such establishments in the allied countries was at first a serious drawback to any increased output of the required munitions of war.

It was then seen that the existence of a well-organized coal-tar industry is one of the first essentials of national defence. Without an adequate supply of coal-tar products no nation can nowadays be self-contained and capable of maintaining its independence in arms without external help. Then arose the public outcry for the development and protection of "key industries." Outside the Germanic alliance each civilized nation, whether belligerent or neutral, strove to set its house in order as regards the production of synthetic dyes, this branch of manufacture being, on account of the above-mentioned facts, a key industry of fundamental importance. Reports of the action taken by the various nations have appeared from time to time in the public press and in official publications of the respective Governments, and these notices are recorded in the pages of our Journal during the past two years.[1]

As all civilized countries are coal consumers, and some are also coal producers, it is evident that a determined bid will be made by each industrialized nation for the supply of its own synthetic dyes and other coal-tar derivatives. To this impending menace to their monopoly the German dye-producers reply by opposing a united front, made up by combining their three existing syndicates in a huge trust, capitalized at more than £11,000,000 sterling. Assuming that other nations persist in their determination to develop their colour industries, then it may be predicted with considerable certainty that the new epoch in the history of coal-tar dyes will find this industry in a condition similar to that of the brewing and distilling trades. In these industries the wants of each country in the way of alcoholic beverages are supplied by the brewers and distillers of the same nation. Only the choicest vintages and the most highly-prized malt liquors find their way across the tariff walls to foreign consumers. It can scarcely be doubted that this will very soon be the condition of trade in the synthetic dye and drug industries. The local demand will be satisfied mainly by local producers, but certain very profitable specialities will command a world sale. In the competition for this foreign trade German manufacturers will for many years have tremendous advantages arising from the possession of well-organized colour factories, generously equipped research laboratories, comprehensive libraries, carefully compiled records, and an amenable personnel of thoroughly trained research chemists working under highly qualified direction in a scientific atmosphere. Added to these are the valuable material assets of cheap bromine, potash, and other essential chemicals.

[1] Great Britain, *J.*, 1914, 1199; 1915, 73, 133, 171, 218, 271, 700. U.S.A., *J.*, 1914, 914, 1178, 1230; 1915, 133, 604, 954, 1182; 1916, 885. France, *J.*, 1915, 1240. Japan, *J.*, 1915, 954; 1916, 37. Russia, *J.*, 1915, 273.

It cannot in fairness be expected that other countries, which have hitherto neglected the factors which make for success in these highly technical industries, can hope immediately to divide the chief prizes with that nation which has assiduously developed each asset, whether material or personal, for more than forty years. Although considerable determination is being manifested on all sides, there is much leeway to make up.

Another point which has recently attracted attention is the circumstance that the synthetic dye question is in reality part of a much larger problem, the conservation of our resources in fuel. Coal and other combustibles are frequently burnt in a shamefully wasteful manner, no attempt being made to collect and utilize the escaping by-products. The economical combustion of our carbonaceous fuels, such as coal, lignite, peat, wood, etc., and the systematic recovery of the by-products, ammonia and tar, is the first essential step towards the establishment of a flourishing industry of synthetic dyes, drugs, and other fine chemicals. Where fuel is wasted, tar products and their derivatives can never be manufactured cheaply and efficiently.

Intermediate Products required in Colour-making.

The immediate products of coal-tar distillation, forming the basis of the synthetic colour industry, constitute a small group of substances, of which the following furnish the very great majority of the so-called coal-tar dyes. These direct coal-tar products — benzene, toluene, xylene, naphthalene, anthracene, phenol, cresol, carbazole, and a few others of minor importance—must usually be converted into more complex derivatives, from which the colours are ultimately produced. These intervening materials are conveniently termed "intermediate products," or, more shortly, "intermediates."

Before the war it was in the production of these essential intermediates that German chemical technologists excelled to the extent of creating a monopoly in this branch of chemical manufacture. The dye-makers of other nations then depended almost entirely on the German supply of these products, and non-German dye-making consisted largely in the assembling of intermediates and the conversion of these substances into finished dyes. Accordingly, it is to the manufacture of intermediates that attention is being chiefly directed by would-be founders of dye factories. If only the difficulties attending the commercial production of intermediates are mastered, a supply of the derived dyes will in most cases be assured.

It will therefore be a useful preliminary to consider recent advances in the production of intermediates.

Nitro-compounds.

The manufacture of aromatic nitro-derivatives has assumed enormous dimensions, owing to the prodigious quantities of trinitrotoluene and picric acid employed as high explosives. After the war these materials will be needed only in much smaller quantities, but the nitrating plants and the practical experience gained will both be utilizable in the production of nitro-compounds required for colour-making and other peaceful objects.

Trinitrotoluene is now being manufactured by the two- and three-stage processes, each of these methods having its supporters.[2]

Picric acid is most frequently prepared by the nitration of phenol, whether distilled from coal-tar or synthesized from benzene. The nitration is effected either by a mixture of nitric and sulphuric acids or by sodium nitrate and sulphuric acid.[3] Great improvements have recently been made in the production of picric acid from dinitrophenol obtained by hydrolysis of chlorodinitrobenzene, a substance readily procured by the successive chlorination and dinitration of benzene. The final product is a well-crystallized picric acid of high density which is easily freed from the waste acid of nitration.

Plant has been devised for continuous nitrations, whereby toluene can be nitrated to mono-, di-, or tri-nitrotoluene in one operation, the determining factor being the relative rates of flow of toluene and mixed acid.[4]

Sulphonation and Sulphonic Acids.

For the purpose of furnishing synthetic phenol, benzene is now being sulphonated on a very extensive scale. The tedious method with ordinary concentrated sulphuric acid can now be accelerated by the employment of fuming acid (oleum). Sodium benzenesulphonate is obtained either by salting out or through the lime salt; both methods are being used industrially.[5]

The monosulphonation of quinol—a substance very prone to yield its disulphonic acid—is effected by heating on the water bath with a slight excess of concentrated acid diluted with 7 % of water in a vessel connected with a suction plant.[6]

Dehydrothio-*p*-toluidine and primuline sulphonated with sulphuric acid at high temperatures give sulphonic acids differing from those obtained with fuming acid. Aminothiazoledisulphonic acids having a sulphonic group in the ortho-position to the amino-group are obtained

[2] *J.*, 1916, 655. [3] *J.*, 1915, 1082.
[4] Borrmann, *Zeits. angew. Chem.*, 1915, **28**, 377. [5] *J.*, 1915, 1082.
[6] Pinnow, *Zeits. Elektrochem.*, 1915, **21**, 380; *J.*, 1915, 1083.

by the baking process from the monosulphonic acids and one molecule or more of sulphuric acid at high temperatures, preferably *in vacuo*. The diazo-derivatives of these disulphonic acids, coupled with aceto-acetanilide, give pure fast yellow shades on cotton.[7]

Alkali Fusions.

This operation is of prime importance in the manufacture of phenols, naphthols, and their sulphonic acids. The older method of fusion in an open pan is frequently displaced by the more modern process of heating under pressure with strong caustic soda solution. This procedure will become increasingly practicable as the output of trustworthy autoclaves is increased.

The caustic soda fusion of sodium benzenesulphonate to phenol is carried out in open pans with satisfactory results[8]; β-naphthol, on the other hand, is more economically produced by heating sodium β-naphthalenesulphonate with strong caustic soda solution under pressure at temperatures approaching 300° C. A product of high quality, suitable for pharmaceutical use, has been obtained by the open pan fusion, but the amount of caustic soda used is excessive if β-naphthol is to be produced at the price prevailing before competition was stopped by the war.

Sodium naphthalene-β-sulphonate heated to 300°–330° C. for fifteen hours with its own weight of caustic soda solution (sp. gr. 1·383) gives a good yield of β-naphthol free from coloured oxidation products.[9]

A third alternative is to combine the two processes by the use of a fusion vessel which can first be heated as an open pan and then subsequently closed and used as an autoclave. α-Naphthol is also preferably prepared by the autoclave method.

Reductions.

Strenuous efforts have been made recently to ascertain the most suitable working conditions for reducing aromatic nitro-compounds with hydrogen or gaseous mixtures containing hydrogen in the presence of catalysts. These reactions are carried out at high temperatures, sometimes under pressure in the presence of water with iron turnings as catalyst,[10] and sometimes in the absence of water, under the ordinary pressure. With a copper catalyst produced by reducing the carbonate,

[7] F. Bayer, Ger. Pat. 281048; Fr. Pat. 473766; *J.*, 1915, 545, 711.
[8] *J.*, 1915, 1082.
[9] Akt.-Ges. f. Anilinfabr., Fr. Pat. 469040, *J.*, 1914, 955.
[10] Ger. Pat. 281100, *J.*, 1915, 543.

formate, oxalate, or nitrate with hydrogen or carbon monoxide below red-heat, reduction of a nitro-derivative such as nitrobenzene is effected by hydrogen at 200° C., or even below this temperature. Higher temperatures are unsuitable, leading to impure reduction products and poisoning of the catalyst. The copper may be used alone or on pumice, asbestos, or kieselguhr, and such activators as alkalis, magnesia, or alumina may be employed.[11]

Nitro-compounds volatile in steam are carried in a vaporous condition by this medium, together with hydrogen, over heated catalysts. An almost quantitative yield of aniline is obtained by passing nitrobenzene, steam, and hydrogen at 120° C. over finely divided nickel.[12]

Recent patents show that the chemists of the Badische Company are still attacking resolutely the problem of manufacturing aniline and other aromatic amines by reduction of nitro-compounds with hydrogen in presence of catalysts. The carefully washed precipitate obtained by adding hot aqueous caustic soda to a solution containing the nitrates of copper, magnesium, and silver is mixed with lumps of pumice stone and sodium silicate and the pasty mass heated to 200° C. in hydrogen. Aniline is produced by passing nitrobenzene vapour and hydrogen over this catalyst at 200°–210° C.[13] A catalyst made by mixing together pumice stone, strong sodium silicate, and the carbonates of copper and zinc, and reducing at a low temperature, is used in conjunction with nitrobenzene, water vapour, and carbon monoxide or gases containing carbon monoxide. At 200°–210° a good yield of aniline is produced.[14]

A solution of sulphur in aqueous sodium sulphide has proved to be a useful reducing agent in Flürscheim's method of converting *m*-dinitrobenzene into *m*-nitraniline, the starting-point for the high explosive, tetranitraniline. This reagent is now recommended for the preparation of aromatic diamines. The monamine from which the diamine is to be derived is first coupled with diazobenzenesulphonic acid, and the resulting azo-derivative reduced with sulphur and sodium sulphide under pressure. Thus *p*-aminodiphenylamine is readily obtained from *p*-sulphobenzeneazodiphenylamine (Orange IV).[15]

Aminonitro-compounds are obtained on the partial reduction of polynitro-compounds by mixing the latter with hot water and iron filings, and passing in sulphur dioxide until the iron has dissolved.[16]

[11] B.A.S.F., Ger. Pat. 282568, *J.*, 1915, 708.

[12] Meister, Lucius, und Brüning, Ger. Pat. 282492, *J.*, 1915, 652.

[13] B.A.S.F., Eng. Pat. 5692/1915, *J.*, 1916, 970.

[14] Eng. Pat. 6409/1915, *J.*, 1916, 970. Compare Eng. Pat. 13149/1914, *J.*, 1915, 790.

[15] Cobenzl, *Chem.-Zeit.*, 1915, **39**, 859; *J.*, 1916, 106.

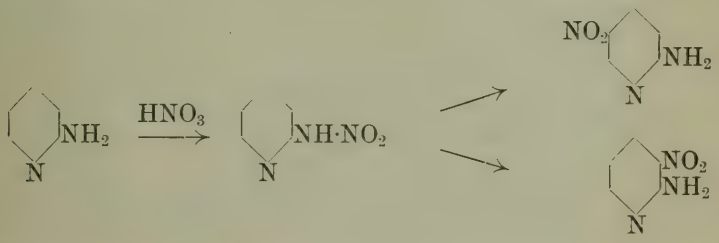
[16] Pomeranz, Ger. Pat. 289454, *J.*, 1916, 415.

Remarkable reducing actions on aromatic and heterocyclic substances have been effected by hydrogen in the presence in colloidal solution of metals of the platinum group.[17]

Condensations.

The great and still increasing demand for toluene has led not only to economies in its production from coal tar and its recovery from coal gas, but also to processes for synthesizing it from the more plentiful hydrocarbon benzene. Methyl chloride, from methyl alcohol and hydrogen chloride in presence of zinc chloride, is passed through benzene in presence of aluminium chloride and iron filings heated to 45°–55°. At these temperatures the homologues of benzene higher than toluene are not produced.[18]

Sodamide, which is required in the synthesis of indigotin from phenylglycine, has been utilized in interesting syntheses in the pyridine series. It interacts with this base below 120°, and the initial additive product when decomposed with water gives a 70% yield of 2-aminopyridine. With 2-methylpyridine and methyl iodide sodamide gives rise to 6-dimethylamino-2-methylpyridine. Further action of sodamide on 2-aminopyridine leads to 2·6-diaminopyridine in good yield. This diamine couples with diazonium salts to furnish azo-dyes. The sodamide reactions go best in toluene, xylene, vaseline oil, or dimethylaniline, access of atmospheric oxygen to be avoided. The nitration of 2-aminopyridine has been fully investigated and found to take place in the following stages :

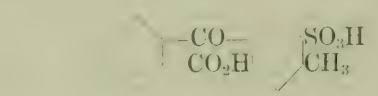


The nitroamine, which is comparatively stable towards acids, slowly undergoes isomeric change into the two nitro-derivatives, the yield of 5-nitro-2-aminopyridine increasing as the temperature rises. Further nitration of this nitro-derivative leads to a new nitroamine, which changes into 3·5-dinitro-2-aminopyridine. Diazotization of 2-aminopyri-

[17] Skita, *Ber.*, 1915, **48**, 1486 and 1685; *J.*, 1915, 1271, and 1916, 35.
[18] Sifton, Eng. Pats. 8886 and 9437/1915, *J.*, 1916, 248.

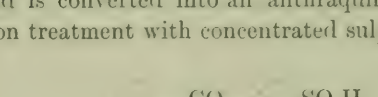
dine in hydrochloric acid leads to 2-chloropyridine and 2-pyridone.[19] These reactions point to possible industrial uses of 2-aminopyridine and 2·6-diaminopyridine.[19]

The synthesis of anthraquinone derivatives from *m*-xylene is effected by condensing this hydrocarbon with benzoyl chloride or its homologues. The product is sulphonated, yielding *as*-dimethylbenzophenonesulphonic acid, which is oxidized to a carboxylic acid (I).



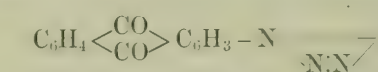
I.

This compound is converted into an anthraquinone derivative (II) by loss of water on treatment with concentrated sulphuric acid.[20]

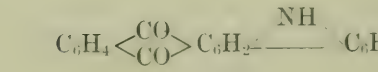


II.

The action of nitrous acid on N-aryl aromatic *o*-diamines leads to stable inert *o*-diazoimines. These products have not hitherto received much attention from industrial chemists. When heated at high temperatures in suitable media, they lose the diazo-group, and are converted into carbazole derivatives. This synthesis, due to Ullmann,[21] has been applied to N-aryl derivatives of *o*-diamino-anthraquinones. On heating the resulting diazoimine an anthraquinonylcarbazole is obtained.[22]



I.



II.

The starting material (Formula I) is obtained by condensing *α*-chloroanthraquinone with aziminobenzene. An isomeride (III) is

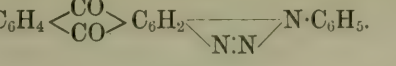
[19] Tschitschibabin, *J. Russ. Phys. Chem. Soc.*, 1914, **46**, 1216, 1236; 1915, **47**, 1286, 1571; *J.*, 1915, 863, 1240; 1916, 352.

[20] Meister, Lucius, und Brüning, Ger. Pat. 285700, *J.*, 1915, 1135.

[21] *Ber.*, 1898, **31**, 1697.

[22] Ullmann and Illgen, *Ber.*, 1914, **47**, 380; *J.*, 1914, 246.

produced by treating with nitrous acid 1-anilino-2-aminoanthraquinone.



III.

These anthraquinonylazimino-derivatives are best converted into the corresponding carbazoles by heating with diphenylamine. The anthraquinonylcarbazoles are yellow substances, dissolving in concentrated sulphuric acid to blue solutions, and yielding red leuco-derivatives in the hydrosulphite vat. The dyeings on cotton are yellow, orange, and light brown shades not sensitive to alkalis.

Substitutions and Miscellaneous Reactions.

A process which might serve in certain instances as an alternative to the caustic fusion method for phenols, consists in heating the aromatic chloro-derivatives with alkali hydroxides and methyl alcohol with or without other solvents. Chlorobenzene yields phenol; α-chloronaphthalene furnishes α-naphthol, and *o*- and *p*-dichlorobenzenes give rise to *o*- and *p*-chlorophenols. In many cases the yields are nearly quantitative.[23]

1·4-Dichloronaphthalene, a valuable raw product for dye-making, results from the interaction of naphthalene and sulphuryl chloride above 100°.[24]

m-Phenetidine has been added to the list of bases available for dye production. It is prepared from *m*-aminophenol by acetylating to *m*-acetylaminophenol, then ethylating and hydrolyzing the resulting *m*-acetylaminoethoxybenzene.[25]

Bucherer's reaction, by which the amino-group is replaced by hydroxyl, has now been extended to aminoazo-dyes.[26] 2-Carboxybenzeneazo-α-naphthylamine furnishes first the same bisulphite additive compound as 2-carboxybenzeneazo-α-naphthol, and this intermediate product subsequently yields the hydroxyazo-compound. Similar results are obtained with 4-sulphobenzeneazo-β-naphthylamine and *p*-hydroxybenzeneazo-β-naphthylamine.

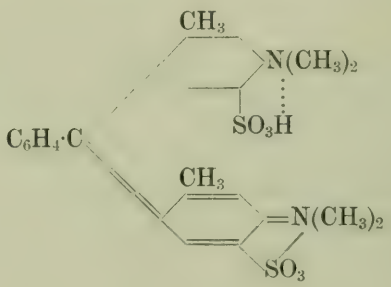
Di- and Tri-phenylmethane Dyes.

The triphenylmethane dyes of the patent blue class owe their extended application to their bluish shade as contrasted with the

[23] Ger. Pat. 281175, *J.*, 1915, 543.
[24] Meister, Lucius, und Brüning, Ger. Pat. 286489, *J.*, 1916, 107.
[25] Reverdin and Lokietek, *Bull. Soc. Chim.*, 1915, **17**, 406; *J.*, 1916, 106.
[26] Voroshcov, *J. Russ. Phys. Chem. Sec.*, 1915, **47**, 1669; *J.*, 1916, 353.

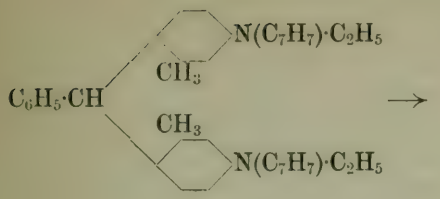
malachite green group, and to their fastness towards alkalis. These valuable tinctorial properties are related to the orientation of substituents in the benzaldehyde residue. In this class of dyes, sulphonic groups or other negative or acidic radicals, such as chlorine, bromine, cyanogen, carbethoxyl, $COOC_2H_5$, or nitroxyl, occupy an ortho-position with respect to the central methane carbon atom. In patent blue itself the ortho-sulphonic group is considered to form an internal salt with a neighbouring amino-group. With the other negative radicals, a similar complex is probably set up by the agency of residual affinity.

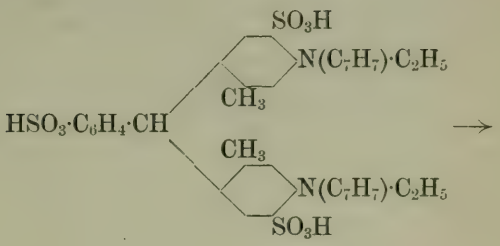
Yellowish green dyes of great fastness are produced by condensing alkyl or aryl derivatives of *m*-toluidinesulphonic acid with benzaldehyde or its homologues not containing a para-amino group and oxidizing the resulting leuco-derivative. The alkyl or aryl *m*-toluidine may also be first condensed with the aldehyde and the resulting leuco-base sulphonated before or after oxidation.[27] In these dyes the sulphonic groups are contiguous to the amino-groups.

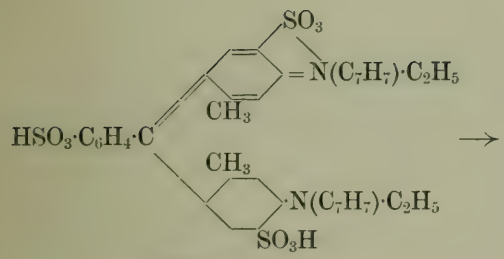


The following is a recently discovered method of increasing the number of auxochromic amino-groups in triphenylmethane dyes. A leuco-derivative of the malachite green series containing a free para-position in the aldehydic group is successively sulphonated, oxidized, and heated with an amine. In the last of these operations the para-sulphonic group is replaced by an amino-radical. The leuco-compound from benzaldehyde and ethylbenzyl-*m*-toluidine, when successively trisulphonated and oxidized, gives a green dye, and this substance, on heating with *p*-toluidine and *p*-toluidine hydrochloride, evolves sulphur dioxide, and becomes converted into a sparingly soluble colouring matter dyeing wool in greenish-blue shades.

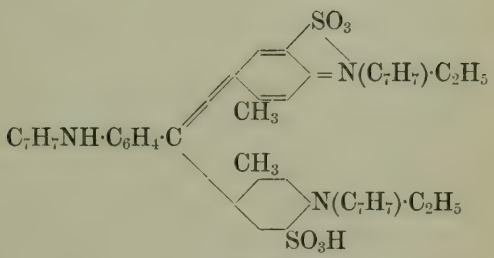
[27] F. Bayer, Fr. Pat. 461810, *J.*, 1914, 195.







Green dye.



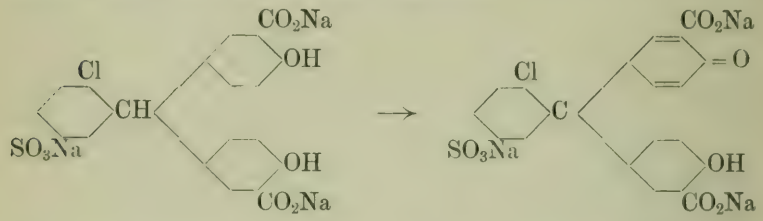
Blue dye.

In these condensations benzaldehyde or 3-hydroxybenzaldehyde-4-sulphonic acid can be first condensed with methyl-, ethyl-, or benzyl-*o*-toluidine, with dimethyl- or diethyl-aniline, or with *o*-cresotic acid. As the amine replacing the sulphonic group, any primary or secondary base may be employed, such as methylamine, benzylamine, aniline, monoalkylanilines, aminophenols, α- and β-naphthylamines.[28]

[28] F. Bayer and Co., Ger. Pat. 287003.

The oxidation of triarylmethane hydroxycarboxylic acids has hitherto been effected by oxidizing agents dissolved in concentrated sulphuric acid, such as nitrosylsulphate, nitric acid, or aromatic nitro-compounds. It has now been found that by employing these hydroxy-carboxylic acids in the form of their salts, alkaline oxidizing agents become effective in producing the colouring matter.

The leuco-compound from salicylic acid and 2-chlorobenzaldehyde-5-sulphonic acid converted into its sodium salt and oxidized with chlorine water yields the corresponding dye.



In these condensations *o*-cresotic acid may replace salicylic acid, and lead peroxide, manganese dioxide, and atmospheric oxygen in the presence of ammoniacal copper solutions are suitable oxidizing agents.[29]

Tetrachlorobenzaldehyde, a valuable intermediate for the manufacture of triphenylmethane colouring matters, is produced by the following series of reactions.

On passing dry chlorine through dry toluene at 12°–15° in the presence of anhydrous ferric chloride, and stirring the mixture thoroughly, trichlorotoluene crystallizes out. This material is melted at 45°–50°, then cooled to 35°, and chlorine again passed in until a molecule has been added, the temperature meanwhile rising to 50°. Only traces of pentachlorotoluene are obtained. Fractional distillation of the chlorination product gives 90 % of tetrachlorotoluene. Further chlorination at 100°–130° in the presence of light, especially ultra-violet rays, yields tetrachlorobenzylidene chloride, $C_6HCl_4{\cdot}CHCl_2$. Tetrachlorobenzaldehyde, colourless needles, m.p. 97°–98°, is obtained by dissolving the preceding compound in concentrated sulphuric acid and pouring the solution into ice water. The crude aldehyde is purified through its bisulphite compound.[30]

When condensed with *o*-cresotic acid, tetrachlorobenzaldehyde gives a leuco-compound oxidizing to a colouring matter giving greenish-blue shades of great intensity and fastness.[31]

[29] F. Bayer and Co., Ger. Pat. 287004.
[30] Cassella, Eng. Pat. 16317/1914, *J.*, 1915, 1203.
[31] Eng. Pat. 13970/1915, *J.*, 1915, 1243.

Condensation of diaminodiarylmethane derivatives and the thio-compounds obtained by the action of sulphur on metadiamines such as *m*-phenylenediamine, 2·4-toluylenediamine, and 2·4-diaminoanisole leads to a series of acridine dyes, ranging from yellow and orange to olive and red.[32]

4·4′-Tetramethyldiaminothiobenzophenone and its homologues are readily prepared from 4·4′-tetramethyldiaminodiphenylmethane and its homologues by heating the latter bases in a reflux apparatus, with crystallized sodium sulphide and sulphur.

$$CH_2[C_6H_4N(CH_3)_2]_2 + 2S = H_2S + CS[C_6H_4N(CH_3)_2]_2$$

The products are useful intermediates in the manufacture of dyes of the auramine group.[33]

Oxazine, Thiazine, and Phenazonium Dyes.

Gallocyanine dyes are converted into their chromium compounds, which can be fixed directly by printing on cotton, wool, and silk without mordants, giving bright, fast shades. Gallamine blue is treated in aqueous solution with sodium acetate and sodium bichromate. The precipitated chromium compound is made into a printing paste with formic acid, hydrosulphite, starch, British gum, and water heated to 90°.[34]

Halogenated gallocyanine dyes are produced by treating gallocyanine and its homologues other than gallanil blue with a halogen (bromine or chlorine). These halogen derivatives and their soluble leuco-derivatives give bluer and faster shades than the parent substances both in dyeing and printing.[35]

Basic safranine dyes result from the condensation of nitrosomethyl-*o*-toluidine and *m*-aminomethyl-*p*-toluidine, this colour giving yellowish-red prints on cotton. A preferable procedure is to produce these safranine dyes by oxidizing a mixture of methyl-*p*-toluylenediamine and methyl-*m*-toluylenediamine.[36]

Several interesting syntheses have been accomplished in the thiazine series. Leuco-methylene blue is conveniently prepared by converting zinc-free methylene blue hydrochloride into the free base by means of moist silver oxide and reducing this base with phenylhydrazine. The

[32] Akt.-Ges. f. Anilinfabr., Ger. Pat. 288841, *J.*, 1916, 356.
[33] B.A.S.F., Ger. Pat. 287994, *J.*, 1916, 352.
[34] Soc. Chem. Ind. Basle, Eng. Pat. 15751/1915, *J.*, 1916, 733.
[35] Soc. Chem. Ind. Basle, Eng. Pat. 14159/1915, *J.*, 1916, 628.
[36] Durand, Huguenin & Co., Ger. Pats. 282346 and 287271, *J.*, 1915, 710; 1916, 171.

leuco-base crystallized from benzene gives an additive compound of this solvent, which on heating gives the pure leuco-base, melting at 159°–160°. The purified leuco-derivative is a strong base, the salts of which are not hydrolyzed in solution. It is not oxidized on exposure to pure air, but oxidizes rapidly in presence of ammonia or hydrochloric acid. It dissolves in ether, acetone, and the alcohols to colourless solutions, but in benzene, chloroform, and other anhydrous solvents to deep red solutions. Neutral oxidizing agents have no effect on the leuco-base until the solution is acidified, when methylene blue is regenerated.[37]

Monophenyl methylene blue (phenyltrimethylthionine) has been prepared by successively condensing thiodiphenylamine with methylaniline by the action of ferric chloride and treating the nitrate of the intermediate product with dimethylamine in alcoholic solution. Replacement of a methyl group by phenyl in methylene blue does not lead to a greener shade of colour.[38]

An elegant synthesis of methylene blue is effected by warming together in glacial acetic acid thiodiphenylamine and bromine. The brownish red crystalline precipitate of phenazthionium perbromide is treated with alcoholic dimethylamine, the perbromide disappears, and from the blue solution methylene blue separates in lustrous needles, the yield being almost quantitative.[39]

Azo-Dyes.

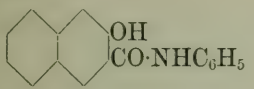
Azo-dyes, the largest section of synthetic colouring matters, still absorb the attention of many workers. The ease with which new intermediates can be produced and the continued fruitfulness of the diazo-reaction account mainly for the developments still taking place in this group of dyes. Although no epoch-making discoveries have been published during the period under review, the work of improving existing azo-dyes has progressed considerably.

Azo-colours are generally true dyes in the sense that they are soluble substances applied to the textile fibres from a suitable dye bath in which they were previously dissolved. With the more soluble azo-dyes especially this dyeing process is readily reversed, leading to a want of fastness to soap and other scouring agents. Very early in the history of azo-colours another method of application was discovered in which an insoluble azo-pigment was developed on the cotton fibre (Read Holliday and Sons, 1880).

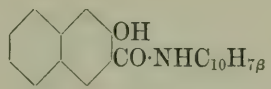
[37] Atack, *J. Soc. Dyers and Col.*, 1915, **31**, 183; *J.*, 1915, 1005.
[38] Kehrmann, *Ber.*, 1916, **49**, 1013; *J.*, 1916, 732.
[39] Kehrmann, *Ber.*, 1916, **49**, 53; *J.*, 1916, 353.

Developed Azo-Colours.

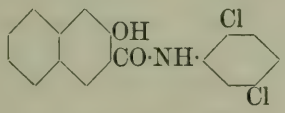
The cotton was first impregnated (padded) with a solution of β-naphthol in caustic soda containing turkey red oil (sulphonated castor oil) and then after drying the fabric was immersed in a solution of a diazotized aromatic amine. β-Naphthylamine diazotized and employed in this way gave a bright red, vacanceine red; α-naphthylamine yielded a port wine tint, α-naphthylamine bordeaux. For many years diazotized para-nitraniline has been used in large quantities in producing on the fibre *p*-nitrobenzeneazo-β-naphthol or paranitraniline red. More recently β-naphthol has been replaced for this purpose by the anilide of 2·3-hydroxynaphthoic acid, a developer giving brilliant shades of considerable fastness. This anilide (I), introduced by the Griesheim Elektron Co. under the technical name of "naphthol AS," has been the subject of much investigation. Its preparation and the production of its homologues and derivatives (II and III) are described in several recent patents.[40]



I.



II.



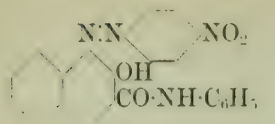
III.

"Naphthol AS" is only soluble in caustic alkalis such as sodium hydroxide or lime water, and its solubility in the latter medium is comparatively slight. With the object of diminishing the alkalinity of the padding solution, 2·3-hydroxynaphthoic acid has been condensed with aminonaphthols, giving rise to dihydroxynaphthalides which dissolve easily in warm dilute aqueous sodium carbonate. From this solution the dihydroxynaphthalides are readily absorbed by unmordanted cotton, which then gives with diazotized amines intense and clear shades of fast azo-pigments.

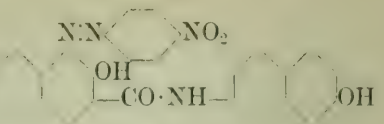
7-Amino-2-naphthol has been employed in this condensation; the fast scarlet azo-pigment with diazotized paranitraniline has the constitution (V), whereas the scarlet from the original "naphthol AS" is represented by formula IV.[41]

[40] Griesheim-Elektron., Eng. Pats. 13237, 23732 of 1912, *J.*, 1913, 1060; 1914, 70.

[41] Synthetic Patents Co., U.S. Pat. 1140747; Ger. Pat. 284997; *J.*, 1915, 709, 1136.



IV.



V.

The diazo-derivatives of *p*-nitro-*o*-toluidine, *o*-anisidine, and α-naphthylamine give with 2-hydroxy-3-naphthanilide (naphthol AS) scarlet, red, and dark red shades respectively.[42]

The diazo and bisdiazo-derivatives of amino- and diamino-anthraquinones, when coupled with arylides of 2·3-hydroxynaphthoic acid, give red lake colours fast to oil. 1-Aminoanthraquinone, diazotized and applied to cotton padded with 2-hydroxy-3-naphthanilide, furnishes a brilliant red fast to light and scouring.[43]

The foregoing examples show that red dyeings are obtained by the use of monoamines of the benzene, naphthalene, and anthraquinone series. The bisdiazonium salts of the para-diamines give rise to violet shades. Of these the colours from dianisidine have received technical application. Dianisidine blue, or azophor blue D, the copper derivative of dianisidinedisazo-β-naphthol, is really a violet pigment, assuming a bluer tint only when fatty acids are present, the colour effect being due to the violet dianisidinedisazo-β-naphthol superimposed on the green copper salt of the fatty acid. The colour is not fast to perspiration. A better result is obtained by coupling diazotized dianisidine with 2·3-hydroxynaphthoic acid or its anilide.[44]

Products of hitherto undetermined constitution have been obtained from the arylides of 2·3-hydroxynaphthoic acid by treatment with formaldehyde in alkaline solution. These substances may also be used in the production of developed azo-colours.[45]

Another basis for developed azo-colours is 5-amino-β-naphthol, the derivatives of which, , where R is an aromatic, acyl or arylsulphonyl group coupled with diazo- and bisdiazo- salts not containing sulphonic groups, give rise to insoluble azo-compounds preferably produced on the fibre. The products are bright in shade and fast to light, washing, and chlorine. Pigments are obtained by producing the colour in the presence of a suitable substratum.

[42] Griesheim-Elektron., Eng. Pat. 17279/1913, *J.*, 1914, 73.
[43] Griesheim-Elektron., Eng. Pat. 10085/1914, *J.*, 1914, 915.
[44] Pokorny, *Chem.-Zeit.*, 1916, **40**, 10; *J.*, 1916, **35**, 415.
[45] Griesheim Elektron., Eng. Pats. 3312 and 3313/1914, *J.*, 1914, 742, 855.

R may be benzoyl, *o*- and *p*-chlorobenzoyl, 2·4- and 2·6-dichlorobenzoyl, *m*-nitrobenzoyl, *p*-toluenesulphonyl, and *p*-chlorobenzenesulphonyl. The condensation is effected by treating 5-amino-β-naphthol in an indifferent medium with the corresponding acid chloride with or without a condensing agent.[46] 5-Amino-β-naphthol is conveniently prepared by Sachs's method,[47] which affords another illustration of the industrial employment of the important reagent, sodamide. β-Naphthol, heated with 1½ parts of this reagent in naphthalene for 1–2 hours at 205°–220°, evolves hydrogen and furnishes 5-aminonaphthol, the yield being nearly 50 % of the calculated amount.

The technical advantage attending the use of the foregoing developed azo-colours lies in the fact that the products are practically insoluble in aqueous solutions of acids or alkalis. A similar advantage is gained with soluble azo-dyes, when these substances are so constituted that they can be rendered insoluble or less soluble by some simply applied after-treatment on the fibre.

Formaldehyde Condensation Products of Azo-Dyes.

One method of producing this increased fastness to washing is based on the great reactivity exhibited by formaldehyde towards the phenols and naphthols and their homologues and substitution products. These condensations form the basis of the process for producing the synthetic resin, bakelite, and arise as chemical changes allied to those involved in the formation of *o*- and *p*-hydroxybenzyl alcohols and their more highly substituted products, the saliretins. This reactivity is even greater with the polyhydric than with the monohydric phenols, the limiting case being that of phloroglucinol, which was shown by Tollens and Clowes to yield quantitatively the insoluble brick-red condensation polymerized product $(C_7H_6O_3)_x$, with aqueous formaldehyde, and even with substances such as Schiff bases, which contain a hydrolyzable methylene group (*Ber.*, 1899, **32**, 2841).

The azo-dyes to which the formaldehyde condensation can be applied are those produced from resorcinol or *m*-aminophenol or a similar reactive phenolic compound. Originally the process was introduced for the purpose of rendering the direct cotton dye, diphenyl black, fast to washing,[48] and the principle has been extended to the case of the vulcan colours introduced by Messrs. Levinstein.

An interesting development of the formaldehyde condensation enables

[46] B.A.S.F., Fr. Pat. 472893, *J.*, 1915, 486.
[47] *Ber.*, 1906, **39**, 3016; *J.*, 1906, 1036.
[48] Geigy, 1899.

the process to be applied to the production of fast prints on textile fibres.[49]

Acetyl-*p*-aminobenzene-azo-resorcinol and hexamethylenetetramine are thoroughly incorporated in a thickening of gum tragacanth, Indian corn starch, olive oil, glycerin, and water, and the mixture is printed, dried, and steamed for a short time without pressure. The print is of a bright orange shade, quite fast even in boiling soap solution, this fastness being due to the insoluble nature of the condensation product. Similar substances can be produced in bulk by treating the dye with boiling formaldehyde solution; different products possibly representing varying degrees of polymerization are obtainable by modifying the experimental conditions.[50]

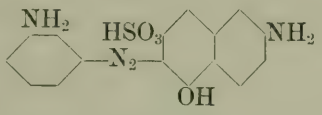
The fastness of substantive dyes having resorcinol as an end component can be increased by treating the dyed cotton fibre. The bisdiazo-compound from *m*-azoxytoluidine coupled with one molecule of *m*-aminobenzoyl-1-amino-8-naphthol-3·6-disulphonic acid, subsequently rediazotized and coupled with two molecules of resorcinol, gives a red which on after-treatment with formaldehyde becomes fast to soap.[51]

An orange dye is obtained by coupling bisdiazotized *m*-azoxytoluidine with J acid (2-amino-5-naphthol-7-sulphonic acid, 1 mol.) and 1 mol. of N-substituted *m*-aminobenzoyl derivative of J acid, bisdiazotizing the resulting disazo compound and coupling finally with resorcinol (2 mols.). The dye is rendered fast by after-treatment on the fibre with formalin solution.[52]

More complex polyazo derivatives containing resorcinol or *m*-aminophenol as end component, have been subjected to this formaldehyde condensation. Acetyl-1·4-phenylenediamine diazotized and coupled with Cleve's acid, gives an azo-derivative which is then diazotized and coupled with the N-*m*-aminobenzoyl derivative of 2-amino-5-naphthol-7-sulphonic acid. This disazo-compound is hydrolyzed and bisdiazotized and finally coupled with 2 molecules of resorcinol. The final tetrakisazo-colour, when dyed on cotton and treated with formaldehyde, gives fast green shades.[53] Sometimes one molecule of resorcinol is replaced by one of α-methylindole or a pyrazolone.[54] Acetyl-4-amino-α-naphthylamine-6-sulphonic acid is diazotized and coupled with α-naphthylamine-6 or 7-sulphonic acid (Cleve's acid), this azo-compound diazotized and coupled

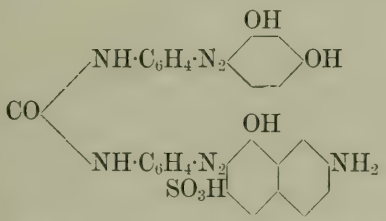
[49] Levinstein, *J.*, 1914, **33**, 573.
[50] Eng. Pats. 29021/1912; 1123, 3427 and 4316/1913, *J.*, 1914, 73, 309, 350.
[51] Eng. Pat. 1436/1913, *J.*, 1914, 197.
[52] Eng. Pat. 1435/1913, *J.*, 1914, 251.
[53] F. Bayer, Ger. Pats. 276140, 276141, 276142, *J.*, 1914, 855.
[54] Eng. Pat. 25547/1913, *J.*, 1914, 1200.

with 2-amino-8-naphthol-6-sulphonic acid (G acid) in alkaline solution. This disazo-compound is diazotized and coupled with α-methylindole or a pyrazolone. The trisazo-compound is hydrolyzed to remove the acetyl group, the product diazotized and finally coupled with resorcinol or *m*-aminophenol. Fast green shades are obtained from these tetrakis-azo-colours by after-treatment on the fibre with formaldehyde solution. The following derivative of J acid, when bisdiazotized and coupled with 2 mols. of resorcinol, gives fine claret red shades especially suitable for union goods.[55]



After-treatment with formaldehyde renders the dyeings very fast to washing without change of colour.

The following disazo-colour derived from *pp*-diaminodiphenylcarbamide



gives on cotton reddish brown shades rendered fast by formaldehyde.[56]

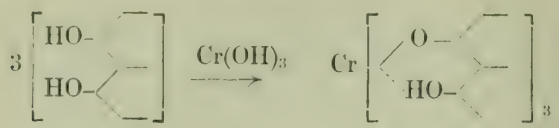
Mordanted Azo-Dyes.

In the earlier phases of the development of azo-colours it was sought to deepen the shades from red to blue and finally to black by increasing the number of azo-chromophors in the molecule. This method of making azo-blacks increased the molecular complexity of the dye and incidentally enhanced its cost of production. The production of wool black has been simplified by the discovery that the shade of certain monoazo-dyes can be greatly deepened providing that these colours are capable of forming coloured lakes with the metallic bases.

The azo magentas from 1·8-dihydroxynaphthalene-4-sulphonic acid and the chromotropes from 1·8-dihydroxynaphthalene-3·6-disulphonic acid (chromotropic acid) are examples of chromed dyes. In these compounds the production of an intensely coloured chromium lake is to

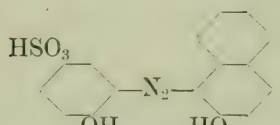
[55] Cassella, Eng. Pat. 6900/1914, *J.*, 1915, 829.
[56] Akt.-Ges. f. Anilinfabr., Eng. Pat. 4072/1915, *J.*, 1915, 1136.

be attributed to the presence in the dye of two hydroxyl groups in the 1·8- or peri-position of the naphthalene nucleus.

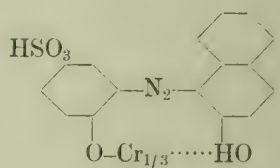


It has since been found that lake formation of this type can occur when the hydroxyl groups are in different nuclei, providing that they are each in the ortho-position with respect to the azo-chromophor joining the two nuclei.

This property leads to the production of chrome mordanted wool blacks from comparatively simple monoazo dyes. Two very successful dyes of this type are diamond black P.V., and palatine chrome black from *o*-diazophenol-4-sulphonic acid coupled with 1·5-dihydroxynaphthalene and *β*-naphthol respectively. The latter dye when unmordanted has the constitution I.



I.



II

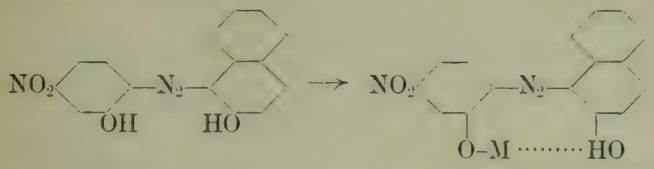
When chromed, the bluish red dye deepens to the black shade of its chromium lake (II).

These intensely coloured lakes are formed only when the hydroxyl-groups have the propinquity indicated by the foregoing formulæ. They are not produced from *p*-diazophenols. 5-Nitro-2-aminophenol, when diazotized and coupled with *β*-naphthol, gives 4-nitro·2-hydroxybenzeneazo-*β*-naphthol, a red substance furnishing intensely coloured lakes with metallic bases. The colours of these lakes are strangely different even when formed from closely related metals. The magnesium lake is crimson, whereas that with zinc is blue; the nickel derivative is purple and the cobalt compound is dark green.[57]

The remarkable properties of these dihydroxyazo lakes are explained in terms of Werner's theory of co-ordination by supposing that each principal valency of the metal displaces one hydrogen atom in a hydroxyl group, whilst an auxiliary valency links up the remaining hydroxyl group so as to form a closed ring containing a metallic

[57] Morgan and Porter, *Chem. Soc. Trans.*, 1915, **107**, 645; *J.*, 1915, 653.

constituent. The foregoing azo-compound represented by I forms metallic lakes represented by II, in which M is a chemical equivalent of the metallic atom.

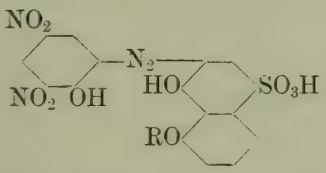


I.—Red azo-compound. II.—Intensely coloured lake.

This assumed ring formation explains (1) the stability and insolubility of the lake, (2) the fact that the contained metallic atom frequently fails to display its ordinary ionic reactions, and (3) the anomalous colour of the lake as contrasted with that of the inorganic compounds of the contained metal.

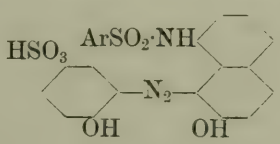
The fastness to light and milling of these mordanted dihydroxyazo-dyes has led to much research in the production of azo-derivatives having the required constitution.

The historical first diazo-derivative obtained by Griess from picramic acid has been utilized in these industrial investigations. Coupled with 8-alkyloxy-α-naphthol-4-sulphonic acids, this diazo-anhydride furnishes the following dyes:



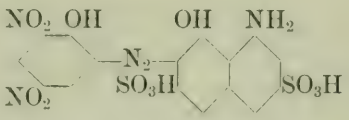
which dyed on wool with bichromate and acid give green shades fast to light and fulling.[58] Olive to brown dyes with chrome mordant are derived from the coupling of diazotized picramic acid and an acyl-4-aminophenol or any substituent having a free ortho position.[59]

Ortho-aminophenol-4-sulphonic acid and the 8-arylsulphonylamino-β-naphthols yield a series of mordant dyes of the constitution



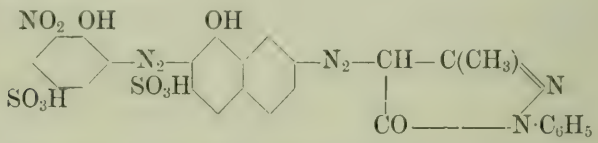
[58] Meister, Lucius, und Brüning, 3rd addn. to Fr. Pat. 361649, *J.*, 1914, 195.
[59] Akt.-Ges. f. Anilinfabr., Eng. Pat. 16592/1915, *J.*, 1916, 686.

giving green shades with chromium base.[60] A striking example of the use of a copper lake is furnished by the coupling of diazotized picramic acid and H acid (8-amino-α-naphthol-3·6-disulphonic acid). The sodium salt of the azo-dye



is mixed with aqueous copper sulphate, and the solution slightly acidified with hydrochloric acid. After stirring for 1–2 hours the solution is neutralized with sodium carbonate. The dark brown copper derivative dyes in black shades from an acid bath.[61]

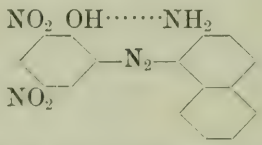
The following disazo dye



from diazotized 2-amino-6-nitrophenol-4-sulphonic acid, 7-amino-α-naphthol-3-sulphonic acid (G acid), and 1-phenyl-3-methyl-5-pyrazolone, furnishes after chroming very fast bronzy-brown shades.[62]

Green disazo dyes on chrome mordant of a similar type are produced by combining ortho-diazophenols with 1·8-aminonaphthol-3·6-disulphonic acid (H acid), diazotizing again and coupling with pyrazolones.[63]

That the co-ordinating group need not necessarily be a second hydroxyl group is seen from the circumstance that diazotized picramic acid, coupled with β-naphthylamine or with acetyl-*p*-naphthylenediamine, gives a violet dye, changed by prolonged boiling with metachrome mordant on wool to fine olive shades fast to milling and light.[64] In these compounds the co-ordinating radical is the adjacent amino group,

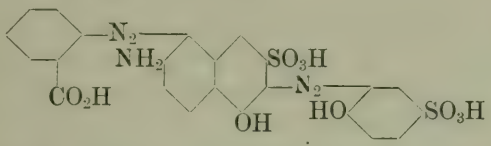


Metachrome brown B is a lake of similar constitution derived from diazotized picramic acid and 2·4-toluylenediamine.

[60] F. Bayer, Ger. Pat. 290078, *J.*, 1916, 532.
[61] Soc. Chem. Ind., Basle, Eng. Pat. 1611/1915, *J.*, 1916, 301.
[62] Sandoz, Eng. Pat. 100472/1916, *J.*, 1916, 733.
[63] Sandoz, Eng. Pat. 17607/1915, *J.*, 1916, 531.
[64] Mensching and Ehrhardt, Eng. Pat. 10716/1915, *J.*, 1916, 301.

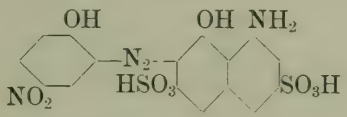
A series of red to dark violet dyes, capable of being chromed to yield bluish black to greenish black shades, is obtained by the use of the so-called J acid (2-amino-5-naphthol-7-sulphonic acid), or its N-alkyl or N-aryl derivatives.

Diazotized anthranilic acid is coupled with J acid or its N-substituted derivatives in acid solution, and the resulting monoazo-dye is combined with *o*-diazophenols in alkaline solution. The simplest member of the series has the following constitution :—



The chrome lakes of these dyes are very fast to light, alkalis, acids, milling, and potting.[65]

An interesting case of lake formation has quite recently been observed with the azo-dye, chrome fast green G



derived from 4-nitro-2-diazophenol and H acid. This dye, boiled with aqueous chromium fluoride till the solution is blue, is treated with sodium acetate, and the solution concentrated, when a red chromium compound separates, which is useless for dyeing. The filtrate on salting out yields needles of a green chromium compound, giving faster shades than those of the original dye.[66]

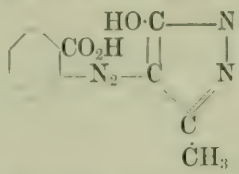
Azo-dyes of the β-diketones and their Condensation Products.

The close interdependence of the manufactures of dyes and pharmaceutical products is illustrated by a tendency manifested in researches on dye-making during recent years, in which advantage is taken of the fact that diazonium salts couple with β-diketone derivatives just as readily as they do with phenols. These β-diketones and their condensation products are needed industrially in the preparation of synthetic drugs, with the result that the technical difficulties of producing these fine chemicals have been largely overcome. The surplus stock of these materials becomes available for use in colour making. The β-diketones and other condensation products react in their enolic

[65] F. Bayer & Co., Eng. Pat. 29567/1913, *J.*, 1915, 899.

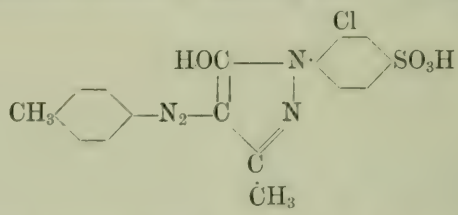
[66] Soc. Chem. Ind., Basle, Eng. Pat. 15064/1915, *J.*, 1916, 831.

form, and thus furnish an adjacent hydroxyl group for lake formation. Yellow chrome mordanted dyes are produced by coupling diazotized anthranilic acid with pyrazolonesulphonic acids or their derivatives.[67]



These dyes of the pyrazolone series may be produced either by coupling the diazo-compound with a pyrazolone derivative having a free 4-position, or by first coupling the diazonium salt with ethyl acetoacetate and then condensing this mixed aliphatic-aromatic azo-derivative with phenylhydrazine, or one of its derivatives.

For instance, diazotized paratoluidine is coupled with ethyl acetoacetate, and the resulting ethyl *p*-tolueneazo-acetoacetate is condensed with 4-chlorophenylhydrazine-4-sulphonic acid. The pyrazolone dye



dyes wool in fast greenish yellow shades from an acid bath.[68]

Cotton colours having pyrazolone components are produced by combining diazotized benzidine-3-sulphonic acid (or 3·3′-disulphonic acid) with 2 molecules of 1-*p*-aminophenyl-3-methyl-5-pyrazolone. This dye and its homologues give brilliant orange shades very fast, especially when developed on the fibre.[69]

A greenish yellow dye, fast to washing and milling, is produced by bisdiazotizing 4·4′-diaminodiphenylsulphide-2·2′-disulphonic acid (thioanilinedisulphonic acid), and coupling the diazo-compound with 2 molecules of acetoacetanilide. The product gives brighter shades than those obtained from the alkyl derivatives of 2·2′-disulphodiphenylsulphide-4·4′-bisazophenol.[70]

The foregoing examples show that hitherto the β-diketo-compounds and their condensation products have been used as substitutes for the

[67] Meister, Lucius, und Brüning, Fr. Pat. 472737, *J.*, 1915, 486.
[68] F. Bayer & Co., Eng. Pat. 8415 1913, *J.*, 1914, 414.
[69] Meister, Lucius, und Brüning, Ger. Pat. 287071, *J.*, 1916, 171.
[70] Akt.-Ges. f. Anilinfabr., Eng. Pat. 100078, *J.*, 1916, 416.

aromatic phenols and reactive amines. In several instances, however, it has been demonstrated that the amino derivatives of the pyrazolone, pyrazole, thiazole, and triazole series are capable of being effectively diazotized. Amino-antipyrine[71] and 4-amino-3·5-dimethylpyrazole yield diazonium salts, which are more stable than the aromatic diazonium salts.

In the thiazole and triazole series the diazo reaction leads speedily to the substitution of chlorine for the amino-group when diazotization is carried out in hydrochloric acid. The stability of the diazonium complex, when attached to a thiazole or triazole nucleus, has been considerably enhanced by the simple expedient of changing the mineral acid.[72] When diazotized in solutions of the oxy-acids—nitric, sulphuric, or perchloric acid—the aminotriazoles and aminothiazoles give rise to diazonium salts having the normal degree of stability. It is at least possible that these non-aromatic diazonium salts may, in the future, play a useful part in the production of azo-dyes.

A substantive cotton colour of the β-diketone series dyeing in pure greenish yellow shades is obtained by oxidizing acetyldehydrothio-*p*-toluidine to the carboxy acid,

$$CO_2H{\cdot}C_6H_4{<}\begin{matrix}N\\S\end{matrix}{>}C{\cdot}C_6H_3(SO_3H){\cdot}NH{\cdot}COCH_3$$

and removing the acetyl group by hydrolysis. The resulting aminothiazolesulphonic acid is diazotized and coupled with acetoacetanilide to produce a dye having the following constitution[73]:

$$CO_2H{\cdot}C_6H_3{<}\begin{matrix}N\\S\end{matrix}{>}C{\cdot}C_6H_3(SO_3H){\cdot}N_2{-}\overset{\displaystyle CH_3{\cdot}C{\cdot}OH}{\overset{\displaystyle \|}{C}}{\cdot}CO{\cdot}NH{\cdot}C_6H_5$$

Substantive Azo-Dyes for Cotton.

One of the unexpected surprises of this group of dyes was the discovery that 2-amino-5-naphthol-7-sulphonic acid and, more especially, its N-substituted derivatives, gave rise to azo-dyes which are substantive on cotton. The other amino-naphtholsulphonic acids only do this when coupled with diazotized para-diamines or other similar components. On this account special attention has been paid to the N-derivatives and azo-compounds of this 2-amino-5-naphthol-7-sulphonic acid (J acid).

[71] Morgan and Reilly, *Trans. Chem. Soc.*, 1913, **103**, 808; 1914, **105**, 435.

[72] Morgan and Morrow, *Trans. Chem. Soc.*, 1915, **107**, 1294; Morgan and Reilly, 1916, **109**, 157.

[73] F. Bayer, Eng. Pat. 25029/1913, *J.*, 1914, 71.

A disazo-dye giving blue shades on unmordanted cotton is produced by coupling diazotized 2·5-dichloroaniline-4-sulphonic acid with 1-amino-2-ethoxynaphthalene-6-sulphonic acid and then diazotizing this azo-compound and coupling with *p*-aminobenzoyl-2-amino-5-naphthol-7-sulphonic acid. Very fast green shades on the fibre are produced by diazotizing this dye and coupling with 1-phenyl-3-methyl-5-pyrazolone, acetoacetanilide, phenol, or resorcinol, or the green may be developed with diazotized *p*-nitraniline.[74]

Mechanism of the Formation of Azo-Derivatives.

Combination with phenols and phenolic ethers takes place most readily with those diazonium salts containing the most "negative" substituents. The diazonium salt of 2·4-dinitraniline is very reactive and couples very rapidly with the ethers of resorcinol and naphthol, even in acetic acid solution. In these circumstances a benzenediazonium salt does not react with the phenol or phenolic ether. On the other hand, with negative groups in the phenolic ether, as in *p*-nitroanisole or *p*-nitroethoxynaphthalene, coupling is hindered and takes place either very slowly or not at all. The following phenols are arranged in the order of their facility for coupling :—phloroglucinol, α-naphthol, resorcinol, β-naphthol, catechol, phenol, quinol, *o*-nitrophenol. This order applies also to their respective ethers. In the diazo coupling with these ethers the products are alkoxyl azo-derivatives, hydroxyl azo-derivatives, or a mixture of the two. It is assumed that this result is due to the initial formation of an additive compound by the addition of the diazohydroxide to a conjugated double linking of the aromatic nucleus.[75]

A more general explanation applicable to all cases of azo coupling is that the diazonium salt (or diazo-hydroxide) first attaches itself to the oxygen of the aromatic alkoxyl or hydroxyl group or to the nitrogen of the aromatic primary, secondary, or tertiary base to form respectively an oxonium or an ammonium salt.

$$C_6H_4H{-}O{-}R + R'{\cdot}N_2{-}OH = C_6H_4H{-}\underset{\displaystyle OH}{\overset{\displaystyle R}{O}}{-}N_2R'$$

I.

[74] Synthetic Patents Co., U.S. Pat. 1150675, *J.*, 1916, 531.

[75] K. H. Meyer, Irschick, and Schlösser, *Ber.*, 1914, **47**, 1741 ; *J.*, 1914, 687.

$$C_6H_4H{-}N{<}\begin{matrix}R\\R'\end{matrix} + R''{\cdot}N_2{-}OH = C_6H_4H{-}\overset{\overset{R\quad R'}{\diagdown\ \diagup}}{\underset{|}{N}}{-}N_2R''$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad OH$$

II.

From the oxonium salt by elimination of water one obtains $R'N_2C_6H_4{\cdot}OR$ and by elimination of ROH the products $R'N_2{\cdot}O{\cdot}C_6H_5$ and $R'N_2{\cdot}C_6H_4{\cdot}OH$. All these cases have been realized in practice.

Similarly from the ammonium salt by elimination of water one obtains $R''N_2{\cdot}C_6H_4{\cdot}NRR'$, and by elimination of ROH one arrives at $R''N_2{\cdot}NR'{\cdot}C_6H_5$ and $R''N_2{\cdot}C_6H_4{\cdot}NHR'$. Instances of these three reactions have also been observed; the third occurs when dibutyl- or di-*iso*-amylaniline is coupled with diazobenzenesulphonic acid, one of the heavy alkyl groups being eliminated.[76]

Sulphur Dyes.

Taken in its widest sense this section would include all dyes containing sulphur in the chromophoric group. The thiazines (methylene blue) and thiazoles (primuline group) have, however, already been discussed, and there remains the sulphide dyes and their allies of the hydron blue class. Recent advances in this group of synthetic dyes have been made in three directions: (1) further development of the valuable hydron blue dyes; (2) improvements in the production of yellow sulphide dyes; (3) the application of sulphide colours to the dyeing of animal fibres.

Hydron blue is not only a valuable vat dye, rivalling indigo in shade and permanence, but it is also of technical interest as affording another industrial use for carbazole, a direct coal tar product, which had hitherto received little attention. Nitrosophenol and carbazole are condensed in concentrated sulphuric acid yielding carbazole-indophenol. Intense thionation of this product with sodium sulphide and sulphur leads to hydron blue, which, although insoluble in sodium sulphide, is amenable to vat dyeing by the hydrosulphite process.

The carbazole-indophenolsulphonic acids are produced either by condensing nitrosophenol and the sulphonic acids of carbazole and N-alkylcarbazoles in concentrated sulphuric acid or by treating with sulphite or bisulphite the unsulphonated indophenols of carbazole and its N-alkyl derivatives. Prolonged thionation of these blue sulphonated

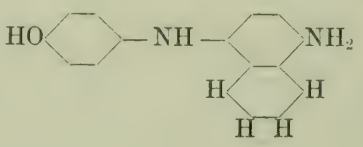
[76] Karrer, *Ber.*, 1915, **48**, 1398; *J.*, 1915, 1241.

indophenols or their leuco-compounds with alkali polysulphides leads to dyes giving blue shades on cotton very fast to light and to chlorine.[77]

Carbazole-indamines resemble carbazole-indophenol in their interaction with alkali polysulphides. The latter carbazole derivative on moderate treatment with the thionating agents furnishes a sulphide blue dyeing cotton from a sodium sulphide bath. More intense thionation gives the vat dye, hydron blue, insoluble in alkali sulphide.

The carbazole-indamines are produced by condensing with carbazole in concentrated sulphuric acid the arylsulphiminoarylene-chloroimides $ClN{:}R{:}N{\cdot}SO_2Ar$, where R is C_6H_4 or $C_{10}H_6$. The product obtained by thionating these indamines or the leuco-indamines with alkali polysulphide, either with or without copper or copper compounds, is a mixture of (1) a true sulphide dye soluble in warm aqueous sodium sulphide, giving intense blue shades on cotton, and (2) a vat dye of the hydron blue class, insoluble in aqueous sulphide, but giving similar tints of great fastness from a hydrosulphite vat.[78]

A significant extension of colour research to derivatives of tetrahydronaphthalene has been recorded during the present year. The indophenol or leucoindophenol (I) derived from *p*-aminophenol and *ar*-tetra-



I.

hydro-α-naphthylamine on thionation yields a sulphide colour dyeing unmordanted cotton in fast pure blue shades from either a sulphide or hydrosulphite bath.[79] For many years Bamberger's hydrogenized naphthalene derivatives have been regarded as laboratory curiosities, but cheaper sodium and amyl alcohol will ultimately render them industrial possibilities.

N-Substituted carbazoles, where the substituent may be an alkyl, aryl, or aralkyl group, are being utilized in improving the qualities of yellow sulphide dyes. The foregoing carbazoles when heated with sulphur at high temperatures, preferably in presence of benzidine, tolidine, or other adjuvant used in making sulphide yellows, give rise to thionated dyes of pure yellow shades and very fast to chlorine.[80]

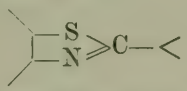
[77] Cassella, Fr. Pat. 462316, *J.*, 1914, 247.
[78] Soc. Chem. Ind., Basle, Eng. Pat. 15949/14, *J.*, 1915, 955.
[79] Buff and Thauss, U.S. Pat. 1175230, *J.*, 1916, 531.
[80] Cassella, Fr. Pat. 475014, *J.*, 1915, 1085.

Yellow sulphide colours fast to chlorine and dyeing on unmordanted cotton, are obtained by heating aromatic bases with sulphur and benzidine. The dye from ethylaniline and benzidine gives pure greenish yellow shades.[81]

Yellow and orange sulphide dyes giving bright shades on unmordanted cotton, very fast to washing, are produced by heating with sulphur at 200°–220° a mixture of *p*-aminoacetanilide, formanilide, or formyltoluidine and benzidine, tolidine, or dianisidine.[82]

Yellow sulphide dyes can also be obtained by fusing with sulphur (1–2 mols.) primary diamines of the diphenyl series, methylated in the nucleus or their halogen substitution products, with or without benzidine. In the case of tolidine, the addition of benzidine is essential.

The presence of alkyl or formyl groups in all these processes for yellow sulphide dye supports the view that these colours are thiazole derivatives containing the chromophor



Sulphide dyes suitable for wool-dyeing are obtained by fusing with sulphur and an alkali α-naphthylamine-4·8-disulphonic acid or α-naphthylamine-4·6·8-trisulphonic acid. The colouring matter is precipitated from hot neutral or alkaline solutions by oxidation with a current of air. Blue shades on wool are obtained from an acid bath.[83]

Sulphide dyes are applied to wool and union goods, furs, feathers, and artificial silk, by reducing them with an alkali sulphide in the presence of an alkali sulphite and a neutral ammonium salt.[84]

An interesting observation has been made in regard to the oxidation of thiodiphenylamine in the presence of aniline. In addition to dithiotetraphenylhydrazine,

$$S<\begin{matrix}C_6H_4\\C_6H_4\end{matrix}>N{\cdot}N<\begin{matrix}C_6H_4\\C_6H_4\end{matrix}>S$$

—a colourless substance—there was produced a colouring matter isolated in the form of its double zinc chloride. The free base, which was reddish-yellow, is regarded as thiodiphenoquinoneanil—

$$C_6H_4<\begin{matrix}S\\N\end{matrix}>C_6H_3{\cdot}C_6H_4{\cdot}O$$

[81] Jaeckel, U.S. Pat. 1140745, *J.*, 1915, 709.

[82] Wyler and Littlewood, Eng. Pat. 4035/1915, *J.*, 1916, 463.

[83] Kalle, Fr. Pat. 471230, *J.*, 1915, 171.

[84] Lodge and Evans, Eng. Pats. 29852/1913, 19473 and 23386/1914, *J.*, 1915, 135, 223, 277.

The hydrochloride forms green needles, and dyes wool and silk in green shades, fast to washing with water, and changing to reddish-violet with bases. Ammonium sulphide produces the leuco-compound.[85]

Vat Dyes.

The dyes of this group may be divided into three classes: (1) indigo and indigoid dyes; (2) indanthrene and its analogues; (3) hydrone blue and its allies. The third of these classes has already been dealt with under sulphur dyes, because of the similarity in the mode of preparation of the hydrone and sulphide dyes.

1. *Indigo and Indigoid Dyes.*

Indigo still retains its position as the premier blue dye for wool. The stoppage of the supply of German synthetic indigo has given a new impetus to the cultivation of the indigo plant. In British India the total area of land under indigo during the season 1914–15 was 148,400 acres, whereas in the following year, 1915–16, the area devoted to this product was 314,300 acres. The total yield of indigo for 1915–16 is 39,900 cwt., as against 25,200 cwt. for 1914–15.

As regards attempts to produce synthetic indigo in countries other than Germany and Switzerland, it can scarcely be claimed that this dye has hitherto been produced during the war (1914–15) on an industrial basis, although encouraging results have been obtained in the laboratory and on a semi-works scale.

In August of 1916 Messrs. Levinstein acquired the Ellesmere Port factory of Meister, Lucius, und Brüning, built for the purpose of manufacturing synthetic indigo in England, as a consequence of the British Patent Act of 1907. These works, which are now running satisfactorily under the new management, are producing indigo of excellent quality in large quantities.

The process most favoured at present is the synthesis starting from benzene. Not the least difficult steps in this synthesis are the making and handling of large quantities of sodamide and the application of this reagent to the phenylglycine melt. The production of large quantities of sodamide will be a great boon to the manufacturer of fine chemicals, for this substance is a synthetic agent of great potentialities. Instances of its application are recorded in other sections of this report.

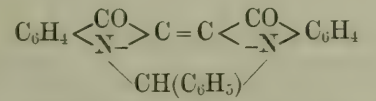
It has recently been demonstrated that indigotin suspended in dilute caustic soda in the presence of active nickel is rapidly reduced by

[85] Pesci, *Gazz. Chim. Ital.*, 1916, **46**, I, 103; *J.*, 1916, 415.

hydrogen at 60°–80° C. The catalyst can be separated by filtration, and the indigo-white solution thus prepared is free from excess of reducing agent. The activity of the nickel for this reduction is retained after one year's immersion in water. The reduction may be promoted by heating under pressure.[86] This process is applicable to the production of leuco-derivatives of other vat dyes, and yields these substances free from hydrosulphite or any other reagent employed in the older vats. In the case of indigo, the alkali may be replaced by lime, or a neutral vat may be employed, but in the latter instance the reaction is much slower. These results are very suggestive, inasmuch as a diminution in the alkalinity of the vat would greatly increase the value and applicability of vat dyes.

Noteworthy extensions in the production of indigoid dyes have recently been made by condensing the halogenated derivatives of 3-keto-2-hydro-1-thionaphthene with pheno-hydroxynaphthocarbazoles, the products being further improved by bromination. Vat dyes giving deep blue to black shades are obtained by condensing isatin α-derivatives with acyl derivatives of the heteronuclear aminonaphthols. A vat dye giving fast black shades is produced by condensing isatin-α-anilide and 2-benzoylamino-5-naphthol in the presence of acetic anhydride.[87] More favourable results are obtained with halogenated isatin derivatives—for example, with 5-chloroisatin-2-*p*-chloranilide.[88]

A description recently given of the newly introduced indigo yellow dyes shows that indigo and benzoyl chloride interact in molecular proportions in a neutral solvent in the presence of copper powder to give rise to indigo yellow 3G—



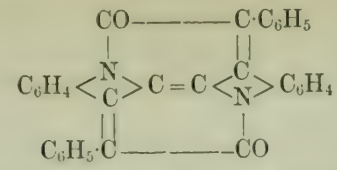
The dibromo-derivative, ciba yellow G, when treated with reducing agents (sodium hydrosulphite or hydrosulphide) in an indifferent solvent (alcohol), and in the absence of caustic alkali, yields ciba yellow 5R.

When phenylacetyl chloride replaces benzoyl chloride in the foregoing condensation a more extensive substitution occurs. The product, lake-red ciba B, is an insoluble pigment incapable of giving vats, but furnishing a soluble dye by sulphonation—

[86] Brochet, *Comptes Rend.*, 1915, **160**, 306; Fr. Pat. 473536, Eng. Pat. 19848 1914, *J.*, 1915, 416, 709, 1047.

[87] Kalle, Fr. Pat. 463772, *J.*, 1914, 416.

[88] Eng. Pat. 22287/1913, *J.*, 1916, 301.



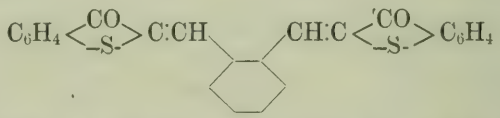
The above constitution for lake-red ciba B shows that both indigoid carbonyl groups have gone, and explains the non-formation of a leuco-derivative in the vat.

Similar products have been obtained from green β-naphthyl-indigo.[89]

An interesting research has been published on complex indigoid dyes containing the group $>CH{\cdot}CH<$ intercalated between the two symmetrical halves of the indigo molecule. The compound

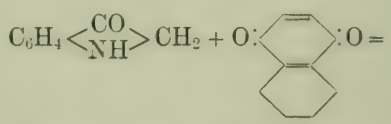
$$C_6H_4<\begin{matrix}CO\\NH\end{matrix}>C{:}CH{\cdot}CH{:}C<\begin{matrix}CO\\NH\end{matrix}>C_6H_4$$

obtained from indoxyl and glyoxal hardly differs in tinctorial properties from indigotin. The employment of maleic aldehyde in place of glyoxal leads to the interposition of the group $>CH{\cdot}CH:CH{\cdot}CH<$ between the indigo residues. Phthalic and terephthalic aldehydes give similar products with hydroxythionaphthene, the former having the constitution—

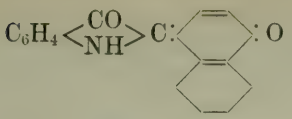


This substance is an orange-red pigment giving a colourless vat, which oxidizes first to blue and then to the original orange-red. The blue stage probably corresponds with an intermediate quinonoid phase of reduction.[90]

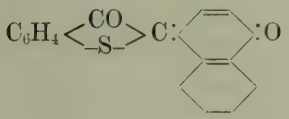
The condensation products of indoxyl and hydroxythionapthene with the α- and β-naphthoquinones and their sulphonic acids are being studied with regard to their utilization as vat dyes of the indigo (I) and thioindigo (II) series[91]—



[89] Engi, *Chem.-Zeit.*, 1914, **38**, 199; *J.*, 1914, 854.
[90] Friedländer and Risse, *Ber.*, 1914, **47**, 1919; *J.*, 1914, 687.
[91] Kalle, Ger. Pat. 286151, *J.*, 1915, 1136.



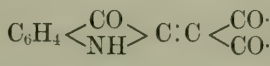
I.



II.

Indigo derivatives consisting partly of open chain groups are obtained by condensing anilides of *o*-diketones with *β*-diketones.

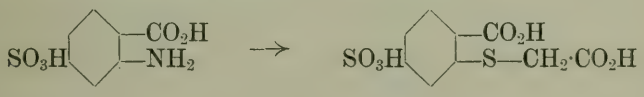
Isatin *α*-anilide and acetylacetone give rise to 2-indole-3-pentanone-indigo—



a cinnabar-red substance reducible with alkaline hydrosulphite, but dyeing in fugitive shades. A similar compound is obtainable from benzoylacetone.

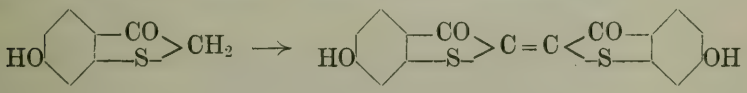
Acetylacetone and thionaphthenequinone anilide give 2-thionaphthene-3-pentanoneindigo, a reddish-yellow substance yielding a sulphonic acid with hot fuming sulphuric acid.[92]

6·6′-Hydroxy- and 6·6′-methoxy-derivatives of thioindigo are conveniently synthesized from 4-sulpho-2-aminobenzoic acid (I)



I. II.

by converting this into sulphothioglycine-*o*-carboxylic acid (II), which on fusion with caustic potash yields successively hydroxyphenylthioglycine-*o*-carboxylic acid and 3·6-dihydroxythionaphthene (III),



III. IV.

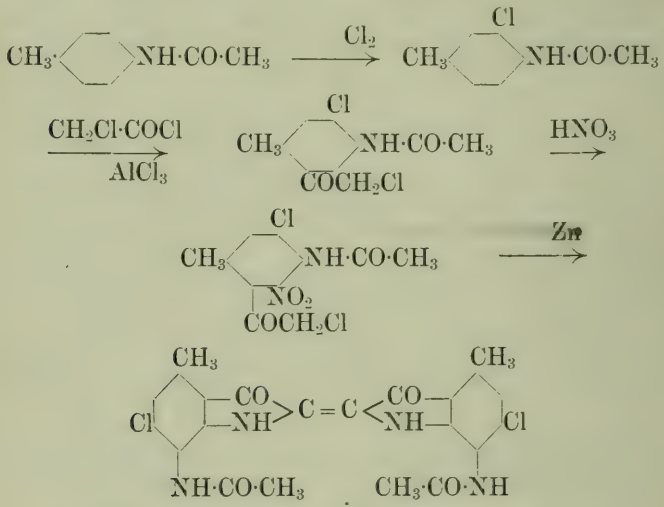
which by oxidation gives 6·6′-dihydroxythioindigo (IV). Treatment of this pigment with methyl sulphate yields 6·6′-dimethoxythioindigo, which is even more readily obtained by starting from

[92] Herzog and Jolles, *Ber.*, 1915, **48**, 1574; *J.*, 1916, 36.

4-methoxy-2-aminobenzoic acid. The colour differences produced by changes in orientation are very marked in this series of substances :—

6·6′-Dimethylthioindigo is orange-red, whereas its 5·5′-isomeride is bluish-violet, and the 4·4′-isomeride violet-red.[93]

An ingenious, although somewhat lengthy, synthesis of substituted indigotins has been introduced by Bodinus, the final step of which consists in boiling a substituted *o*-nitro-*ω*-chloroacetophenone with zinc and 30 % acetic acid. The following example, starting from *p*-acetotoluidide, illustrates the process[94] :—



4·4′-dimethyl-6·6′-dichloro-7·7′-diaceto-aminoindigotin.

The nature of the oxidation products of indigotin obtained under various conditions has been elucidated.

The oxidation products obtained by (1) boiling the pigment in solvents of high boiling-point ; (2) subliming indigo in a limited supply of air (A. G. Perkin, this *J.*, 1907, 464); and (3) oxidation of indigo or isatin with permanganate (Ger. Pats. 276808 and 281050, *J.*, 1914, 1151 ; 1915, 545) are identical, having the composition $C_{15}H_8O_2N_2$. The substance has the constitution I, shown below, and is an anhydro-*α*-isatin anthranilide, this being confirmed by its synthesis (*a*) from isatin chloride and anthranilic acid ; (*b*) from isatin anilide and anthranilic acid ; and (*c*) from *o*-nitrosobenzoic acid and indoxyl.[95]

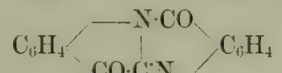
[93] Friedländer, *Ber.*, 1916, **49**, 955 ; *J.*, 1916, 732.

[94] *Chem.-Zeit.*, 1916, **49**, 326 ; *J.*, 1916, 530.

[95] Friedländer and Roschdestwensky, *Ber.*, 1915, **48**, 1841 ; *J.*, 1916, 107.

This substance is insoluble in dilute alkalis, and is reduced by cold hydrosulphite to a leuco-derivative, which is re-oxidized by air to the original yellow colour. Boiling aqueous alkalis hydrolyze the compound into isatin and anthranilic acid.

Isatin is being utilized in the production of a new series of indigoid dyes, in which isatin-α-chloride is condensed with anthranilic acid or other aromatic *o*-aminocarboxylic acid. These products are also obtained by condensing the *o*-aminocarboxylic acid with isatin-α-anil. The anthranilic acid derivative (I) furnishes a light brown leuco-compound dyeing cotton and wool in yellow shades.

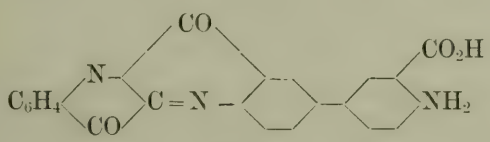


I.

Isatin-α-chloride (2 mols.) and benzidine-3 : 3′-dicarboxylic acid (1 mol.) interact in benzene at 70° to yield a sparingly soluble brownish yellow condensation product (I) having probably the following constitution :—

I.

Benzidine-3·3′-dicarboxylic acid (1 mol.) condensed with the foregoing isatin-α-anil (1 mol.) gives rise to a vat dye (II) forming a light yellow leuco-compound dyeing reddish-brown. This dye may be diazotized on cotton and developed further with β-naphthol to a bluish-red ingrain colour.[96]



II.

Indanthrene and its Analogues.

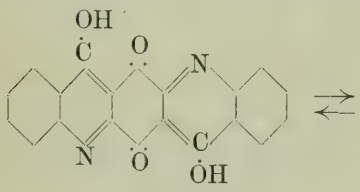
A series of vat dyes giving claret to red shades on cotton is obtained by fusing with alkali hydroxide naphthalene-1·8-dicarboxylic acid imide or the condensation product of acenaphthenequinone and

[96] B.A.S.F., Ger. Pats. 287373 and 288055, *J.*, 1916, 354.

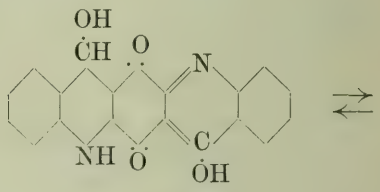
hydroxylamine. These dyes may be alkylated or arylated, or an alkyl- or aryl-derivative of the imide may be fused with caustic alkali. The dye from N-methylnaphthalenedicarboxylic acid imide dyes cotton pure red shades, fast to light and chlorine.[97] Halogenated derivatives of naphthalene-1·8-dicarboxylic acid are also employed.

Similar products are obtained from anthracene-1·9-dicarboxylic acid, the imide of which has a yellow colour and functions as a vat dye, the yellow reduced solutions in alkaline reducing agents dyeing yellow shades on cotton.[98]

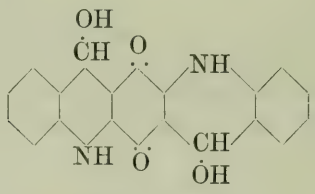
Quinonediacridone, prepared by heating quinonedianthranilic acid with concentrated sulphuric acid at 200°, yields with fuming sulphuric acid (50 % SO_3), a sulphonic acid dyeing silk a fine golden yellow colour from a faintly acid bath. Quinonediacridone (I) itself dyes wool and silk yellow from acid baths. Cotton is dyed only after reduction. There are two leuco-compounds (II and III) representing successive stages of hydrogenation; the latter is reoxidized very slowly.



I.—Orange.



II.—Green.



III.—Violet.

The yellow dye and its sulphonic acid, when exposed to hydrogen in the light, becomes green, this action being very marked with the latter compound.[99]

Mordant dyes for wool of the acridone type have recently been prepared by condensing β-naphthaquinone-3-carboxylic acid with various primary and secondary aromatic amines such as *p*-aminophenol,

[97] Kardos, Ger. Pats. 276357, 276956, *J.*, 1914, 1045, 1084; and B.A.S.F., Fr. Pat. 470560, *J.*, 1915, 171.

[98] Kardos, Ger. Pat. 282711, *J.*, 1915, 710.

[99] Scharvin, *J. Russ. Phys. Chem. Soc.*, 1915, **47**, 1200; *J.*, 1915, 1242.

benzidine, α-naphthylamine, and phenyl-α-naphthylamine. The chrome lakes are deep brown to black in shade, and very fast to light, milling, and potting.[100]

2-Aminoanthraquinone condensed with formaldehyde in the presence of mineral acid yields an orange yellow vat dye giving fast shades to chlorine and washing.[101]

The increase in fastness towards chlorine and washing produced by chlorinating indanthrene has led to many experiments on the chlorination of this vat dye. Treated at 110° C. with chlorine in the presence of a carrier, a chlorinated product is obtained which, by the action of alkali hydrosulphite, is converted into trichloroindanthrene similar in dyeing properties to indanthrene blue GCD (dichloroindanthrene).[102]

Thionyl chloride has been employed instead of sulphuryl chloride in chlorinating indanthrene. By heating at high temperatures the products give faster shades to chlorine than the colours furnished by the chlorinated indanthrenes hitherto obtained.[103]

A vat blue of the indanthrene series has recently been introduced into commerce under the name of chloranthrene blue by British Dyes, Limited. Another British firm, Messrs. Morton, of Carlisle, claim to have produced an indanthrene blue even earlier, in February, 1915.

Further progress in the manufacture of vat dyes has been achieved since the outbreak of war by Messrs. Claus and Co., of Manchester, who are now extending this branch of colour-making in association with Messrs. Levinstein.

Substantive Anthraquinone Dyes.

Considerable activity has been shown during the past two years in the study of the substantive dyes of the alizarin cyanine green and alizarin saphirol group.

Anthraquinone-2-sulphonic acid, when heated with aromatic monamines in the presence of alkali hydroxides or alkyloxides, gives rise to β-arylaminoanthraquinones which on sulphonation yield wool dyes.[104]

The methylation of aminoanthraquinones has been simplified by the discovery that monomethylaminoanthraquinones are readily obtained, uncontaminated with higher methylated products, by treating the

[100] Cassella, Ger. Pat 290064.
[101] Griesheim-Elektron., Ger. Pat. 287907, *J.*, 1916, 355.
[102] Griesheim-Elektron., Ger. Pat. 292127, *J.*, 1916, 832.
[103] Meister, Lucius, und Brüning, Ger. Pat. 287590, *J.*, 1916, 171.
[104] B.A.S.F., Ger. Pat. 288464, *J.*, 1916, 355.

amino-compounds with methyl alcohol in the presence of fuming sulphuric acid.

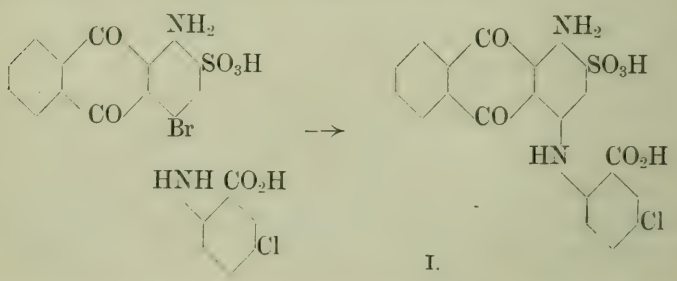
1-Methylaminoanthraquinone is prepared by adding 1-aminoanthraquinone to a solution of methyl alcohol in oleum (65 % SO_3), and then heating the mixture to 200–210°.

This process carried out on *p*-diaminoanthrarufinsulphonic acid leads to *p*-dimethyldiaminoanthrarufinsulphonic acid, an acid dye for wool giving bright and fast shades of blue.[105]

The old method of sulphonating aromatic compounds by means of sulphites, used originally by Piria in producing naphthionic acid, has been revived and applied to the hydroxy- and amino-anthraquinones. Quinizarin (1·4-dihydroxyanthraquinone) treated in this way, preferably in the presence of oxidizing agents, yields quinizarin-2-sulphonic acid. Purpurin (1·2·4-trihydroxyanthraquinone) gives rise to purpurin-3-sulphonic acid. Other polyhydroxyanthraquinones give with sulphites sulphonic acids differing in constitution from those obtained by the ordinary sulphonation process.[106] By this sulphite process the halogen atoms in β-positions of *p*-aminoacylaminoanthraquinone are replaced by a sulphonic group giving useful acid dyes.

These anthraquinone substantive dyes for wool contain, in virtue of their reducible carbonyl groups, the potentialities of vat colours, and in this respect these two classes tend to merge the one into the other. Intermediate products leading either to acid substantive wool dyes or to vat colours are produced by condensing the halogenated α-aminosulphonic acids with anthranilic acid or its halogenated derivatives.

4-Amino-1-bromoanthraquinone-3-sulphonic acid and potassium *p*-chloroanthranilate are condensed to yield potassium 4-amino-1-*p*-chloro-*o*-carboxyanilidoanthraquinone-3-sulphonic acid (I),

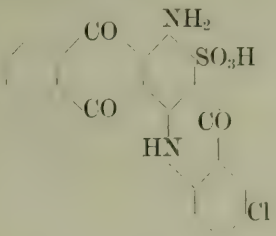


I.

This intermediate product, when treated at moderate temperatures

[105] F. Bayer and Co., Ger. Pat. 288825.
[106] F. Bayer, Ger. Pats. 287867, 288474, 289112, *J.*, 1916, 355.

with 23 % oleum, undergoes dehydration and is converted into a complex acridonesulphonic acid (II),

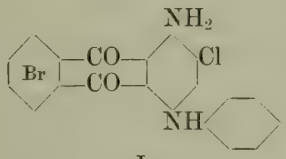


II.

which dyes wool in fast green shades from an acid bath. When digested for many hours with 62 % sulphuric acid at the ordinary temperature, the preceding acridonesulphonic acid and its analogues are desulphonated and hydrolyzed into insoluble coloured substances which can be applied to cotton from a hydrosulphite vat. The acridone from 4-amino-1-bromo-anthraquinone-3-sulphonic acid and anthranilic acid is brominated and desulphonated, the resulting 4-amino-bromo-anthraquinonyl-1·2-acridone gives fast blue shades as a vat dye. Similar results are obtained with the chloro-compound.[107]

The halogenation of anthraquinone dyes conduces to their increased fastness to light and detergents.

β-Chloroanthraquinone successively nitrated and reduced yields α-amino-β-chloroanthraquinone. Dibromination leads to the introduction of one bromine atom in position 4 and another in one or other of the heteronuclear positions 6 and 7. By boiling with aniline (I) or *p*-toluidine, the para-bromine becomes substituted by an arylamino residue,



I.

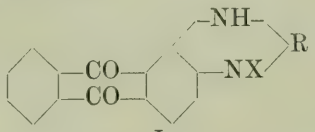
Sulphonation of this product leads to a blue acid dye giving faster shades than when the heteronuclear halogen atom is absent.[108]

Similar dyes are obtained by starting from 1-amino-6- or 7 bromo-anthraquinone, brominating with excess of bromine, condensing the brominated product with hot aniline or other arylamine, and sulphonating the arylamide.[108]

[107] B.A.S.F., Ger. Pat. 287615; Eng. Pat. 17764/1914, *J.*, 1916, 831.

[108] Meister, Lucius, und Brüning, Eng. Pat. 4540/1915, *J.*, 1916, 170.

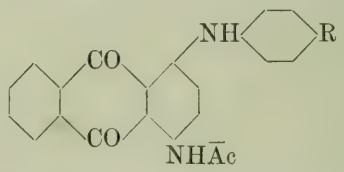
More highly condensed arylamines are produced by condensing anthraquinone-2-sulphonic acid with aniline or *p*-toluidine. The resulting *β*-arylaminoanthraquinone is treated further with the same or a different base in the presence of condensing agents and an oxidizing agent such as a stream of air.



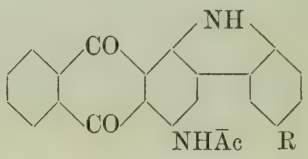
I.

These products have the general formula I where X and R are univalent and bivalent aromatic radicals respectively. When sulphonated with oleum in the presence of boric acid, these substances yield sulphonic acids dyeing wool in fast blue shades.[109]

The *α*-arylaminoanthraquinones substituted by an acylamino-group in the para-position and having the general formula

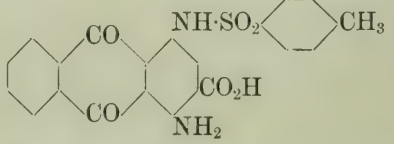


readily undergo oxidation to products containing carbazole groups



These products are vat dyes, and when sulphonated they yield acid wool dyes.[110]

1-*p*-tolylsulphamino-4-aminoanthraquinone-3-carboxylic acid



yields violet and blue lakes respectively when its mono- and di-sodium salts are treated with the corresponding amounts of barium chloride.

[109] B.A.S.F., Eng. Pats. 3347/1915, 100580, 100581, *J.*, 1916, 831.
[110] F. Bayer and Co., Ger. Pat. 288824.

The presence of the sulphonamide group is very beneficial, since 1·4-diaminoanthraquinone-2-carboxylic acid is only partially precipitated by metallic salts yielding unsatisfactory lakes.[111]

This summary of the progress recently achieved in the domain of synthetic dyes and their intermediates is unavoidably incomplete, owing not only to the exigencies of time and space but also because of the difficulty of obtaining precise information of contemporaneous work, much of which is necessarily carried on in secrecy. The task of preparing this compilation is at present rendered more difficult because of the "fog of war" which has descended on almost all the industrialized countries of Europe. Sufficient evidence has been disclosed, however, to prove that a very considerable amount of research in colouring matters is progressing in the principal belligerent nations. These activities may assist the readers of this report, and especially those on the pacific side of the Atlantic, to realize that the creative impulses of humanity are holding their own even on the confines of a chaos within which at present man's destructive agencies appear to be predominant.

[111] Akt.-gesellsch. f. Anilinfabr., Ger. Pat. 287013.

ACIDS, ALKALIS, SALTS.

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The following summary is inevitably tinged by the anomalous position of affairs in Europe. The severance of commercial relations with the Central Powers and the restricted dealings with neutral countries, accompanied by the sudden influx of orders of a special and urgent character, has changed the aspect of the chemical industries. We read of serious impediments to the working of Dutch works arising from the stoppage of imports of pyrites and hydrochloric acid, but after this period of depression we are given to understand that the vitriol works in Holland have been very busy, notwithstanding the difficulties in obtaining raw materials, and that new works are to be erected.

The number of British chemical works included under the Alkali Act has shown a gradual increase—1,305 in 1912, 1,327 in 1913, 1,356 in 1914. In 1915 the total imports of chemicals and allied products are given as £19,344,000 against £12,064,000 and £12,096,000 in 1914 and 1913, the corresponding exports being £1,690,355 against £1,495,322 and £1,705,970. We may therefore conclude that 1916 finds the chemical industry more settled and stable than most of us had dared to hope. The tendency of the manufacturer has been to substitute as far as possible mechanical for manual labour. The erection of new or modified designs of plant with the intention of more intensive production still continues. This intensive system of working seems inseparable from a disproportionate increase in the wear and tear of plant.

One system of vitriol manufacture claims 3 cubic feet chamber space per pound of sulphur against 14 cubic feet in other plants. The conical chambers are water-cooled, and consequently the temperatures are less than half that usually prevailing in the older type of chamber system. Although it is advisable to watch the progress of the newer types of vitriol plant, we believe that, as far as this country is concerned, these new designs are not yet out of the experimental stages, and fundamental alterations, amounting almost to reconstruction, have been necessary in some cases.

The increase in the number of units of plants for the concentration of vitriol is extraordinary, and the experience gained in this direction will have a marked result in deciding future types and the working conditions under which a particular type is indicated. The Kessler system, cascade system, Gaillard tower, and overheat pan have all contributed to the splendid results achieved in the production of the sulphuric acid indispensable for our military needs.

The great opportunity during the war to improve existing products, to scrap old plant, to fit our heavy chemical works with modern plant, and to start the manufacture of new products has not been allowed to pass by unheeded. The progress of Russian heavy chemical trade is reported to be in increased production rather than in methods. In France the only impediments to still greater activity than in pre-war days are the lack of workers and the scarcity of raw material. During the later part of the period covered by this survey it has been possible to mitigate the acuteness of the problem of the supply of raw materials to our Allies. The normal production of vitriol in Germany is stated to be 1,750,000 tons annually, but this has doubtless been much increased by the demands of the munition works. The production in 1912 was given as 1,649,681 metric tons, and in 1913 the imports exceeded the exports by 65,289 tons. The old-established English lead chamber process has to meet the increasing competition of the contact processes. The figures relating to the manufacture of vitriol in the United States, where colossal plants are becoming the rule, are impressive. The production of pyrites in 1915 was 394,124 tons, and the imports for the same year 964,634 tons. The normal consumption of vitriol is above 4,000,000 tons. The present war has exerted a reconstructive activity. At the expense of warring countries, manufacture in the United States has played a most important part in the markets of the world. The total production of 50° B. sulphuric acid was in 1915 3,868,152 short tons.[1] Of this total 1,056,830 tons was by-product acid, mostly from zinc smelting plant.

About 56 % of the vitriol is used in the production of superphosphates and a large amount for sulphate of ammonia.

The vitriol plant at Anaconda is reported to produce 100 tons per day. It consists of a Wedge type of furnace 22½ feet in diameter, twenty-three cooling chambers, six main chambers, and twenty-one Gay-Lussacs (7 feet circular, 38 feet high, built of tiles). The chamber space is 900,000 cubic feet, affording 18 cubic feet per pound S.

[1] *U.S. Geol. Survey*, 1916; *J.*, 1916, 1107.

The Tennessee Copper Company claim 700 tons per day, and give 820 tons as their maximum (50° B.).

In the following synopsis the subject is divided into the groups "Acids," "Alkalis," and "Miscellaneous." The "Salts" will generally be included in the paragraphs immediately following the corresponding acid. Certain patents have been included which in their original intention appear futile, but which possess ideas capable of application to other problems.

Sulphuric Acid.

With regard to the manufacture, as distinct from the plant employed, few suggestions have been made. A claim is made that vitriol can be produced from gypsum or Kieserite at a price equal to that obtained from imported pyrites. The German Imperial Treasury has placed a sum of £175,000 at disposal to erect large works.[2] According to Stanes and Rogé,[3] vitriol may also be obtained from sulphur by roasting with twice its weight of nitre cake. Some use might be found for the acid recovered from "pickle" by concentrating, as suggested by Howl and Perry,[4] to 75 % causing the iron sulphate to be precipitated in an anhydrous form. The modification of Glover towers is the aim of Bithell and Beck,[5] who replace the usual tower by a series of superimposed compartments. Hoefling,[6] with the idea of securing large reaction spaces without obstructed passages, employs tubular packing. Other modes of packing towers are described by Harris and Thomas,[7] who use "stepped" bricks, and by the Accrington Tile Co.,[8] who employ channelled blocks producing long narrow inclined passages. The Curtius[9] (Duisburg) system consists of six towers, replacing the chambers. The gases are introduced at a much lower temperature than is usually employed, into a large tower fed with low nitre acid from later towers in the series. The acid from towers 2, 3, and 4 is brought to 1, where it is denitrated and leaves as a 60 % acid. Nos. 5 and 6 are Gay-Lussacs, the acid from 6 being fed to 5, and then both to 2, or it may be taken direct from 6 to 2. In Hartmann's tower system,[10] the first tower of the series is connected with the last

[2] *Chem. Tr. J.*, Nov. 27, 1915; *J.*, 1915, 1205.
[3] Eng. Pat. 29254 (1913), *J.*, 1915, 227.
[4] Eng. Pat. 5830 (1914), *J.*, 1915, 423.
[5] Eng. Pat. 28743 (1913), *J.*, 1915, 226.
[6] Ger. Pat. 281135 (1912), *J.*, 1915, 611.
[7] Eng. Pat. 7055 (1915), *J.*, 1916, 175.
[8] Eng. Pat. 8152 (1915), *J.*, 1916, 537.
[9] Eng. Pat. 28550 (1913), *J.*, 1915, 904.
[10] Ger. Pat. 284636 (1912), *J.*, 1915, 1090.

but one, and the second with the last, forming two closed acid circulating systems. The last but one serves as the chief Gay-Lussac. If the temperature of the burner gases is not high enough to denitrate the acid of the first tower, acid is drawn from the second tower, fed from the last (auxiliary Gay-Lussac) with lower nitre content. In Klencke's system[11] the gases pass downwards through some or all of the acid-forming towers, thus causing the nitrous vitriol to come into contact with gases of high sulphur dioxide content, causing a vigorous action and affording opportunity for the condensation of the vitriol formed without obstructing the passage of the gases. In Schliebs' system[12] the acid vapours are passed through a series of towers, with a separator interposed between adjacent series, and a portion of the uncondensed gases is returned from each separator by means of a fan to the preceding series of towers. Waggaman[13] supports the lead chamber system as superior as regards both costs and efficiency, and draws attention to the good admixture of gases effected by drawing down through a spiral flue. The use of shaft furnaces for the production of sulphur dioxide is claimed by Koppers.[14] The shaft furnace is provided with a rotating conical grate and rotating ash pan in an enclosed chamber. Air is introduced by a pipe below the grate, and steam is also introduced to reduce the temperature. Any sulphuretted hydrogen produced is burnt. The sulphur dioxide constitutes 10 %, and the oxygen 6–8 % of the resulting gases. Mason's[15] concentration plant consists of six lead pans and forty silica basins, and produces four tons of 95 % acid from 65 % per twenty-four hours, at a cost of 6*s.* 4½*d.* per ton. The total cost of the plant is stated to be £265. The breakage of silica basins in fifteen factories is given as 5 % per annum, and the fuel consumption as being 17 % of the weight of the finished acid. The concentration of vitriol by hot gases is the subject of several patents. The Bernutat[16] system consists of three compartments through which the acid flows in succession, meeting hot gases passing in the opposite direction. Part of the acid from No. 3 and No. 4 flows back to No. 1.[17] Pfannenschmidt and Moss employ a cascade plant of shallow square trays heated by waste heat. The hot acid then falls through a column of hot gases, followed by cold air for cooling in a second chamber. The chambers are provided with

[11] Metallbank, Ger. Pat. 284995 (1913), *J.*, 1915, 1091.
[12] U.S. Pat. 1151294 (1915), *J.*, 1915, 1009.
[13] *U.S. Dept. Agric. Bull.*, 283, 1915; *J.*, 1916, 42.
[14] Ger. Pat. 288322 (1913), *J.*, 1916, 360.
[15] *Met. and Chem. Eng.*, 1915, **13**, 7; *J.*, 1915, 135.
[16] Ger. Pat. 281133 (1914), *J.*, 1915, 611.
[17] Eng. Pat. 13642 (1914), *J.*, 1915, 798.

perforated plates to convert the acid into fine spray.[18] The Norsk Hydro-Elektrisk Kvaelstofaktieselskab describe the concentration of acid under diminished pressure in a series of evaporators, so that a diminishing percentage of water is expelled in each phase of the evaporation.

Another method which appears to be a novel application of a well-known system is suggested by Lennox.[19] Evaporation is produced by a rotating corrugated drum, dipping in troughs for each corrugation. Hot air is drawn through the drum, the acid dripping upon it at the cooler end, and the concentrated acid is withdrawn from the last compartment of the trough at the hot air inlet end.

Two important contributions to concentration plant are to be found in Leitch's patents.[20] In the earlier patent a three-stage process is described. Lead pans are used for concentrating up to 75–80 %, and enclosed iron pans for the final stage, the intermediate vessels being of silica or iron alloy, also enclosed to recover weak distillate. The acid vapours from the intermediate pans are led to a condensing tower and may be used to heat the dilute feed acid. The later addition to the above patent describes the employment of condenser and tower so arranged that the hot vapour from the final pan is conducted to the tower, the dilute acid for concentration to the top of the tower, the heated acid to the first concentrating pan of the cascade, and the hot gases from the top of the tower and intermediate vessels to the condenser. The plant is capable of producing 96–98 % sulphuric acid.

The catalytic production of sulphuric anhydride by means of vanadium pentoxide, and the preparation of the catalyst, is described in a patent[21] by the Badische Co.

The utilization of burnt ore and the extraction of metals from pyritic ores are in many cases intimately bound up with the production of vitriol. A mechanical furnace, combining oxidizing, sulphating, and chloridizing roasting in one unit has been described. The oxidizing is carried out on the upper hearths, and the sulphating and chloridizing on the lower. In the Laist furnace, which is provided with a muffle over the third hearth, the salt is added to the fourth. It is reported that at Anaconda the chloridizing roast is omitted, the salt being added to the leaching vats. The loss of silver is stated to be small.

The production of spongy iron from burnt ore is carried out by reduction brought about by heating in a closed muffle with 25–30 % of coal. At Hoganas, in Sweden, 98 % is stated to be reduced to metal.

[18] Fr. Pat. 474995 (1914), *J.*, 1915, 1142.
[19] Eng. Pat. 23919 (1914), *J.*, 1915, 1054.
[20] Eng. Pat. 1495 and 16001 (1915), *J.*, 1916, 308, 689.
[21] Eng. Pat. 23541 (1913), *J.*, 1916, 833.

In a hydrocarbon gas atmosphere 90 % was reduced in one hour. A furnace of the Wedge type, with six roasting hearths, one drying, and one cooling hearth, is employed. The three upper shelves are of the usual pattern : the three lower are externally heated muffles, oil fuel being used. Pulverized coal is delivered into the upper muffle. A system of vertical retorts has also been tried, and probably will prove to be more easily worked and cheaper than the above.

The Hybinette[22] process of working up pyrites cinders is based upon the fact that copper sulphide is readily soluble in solutions of ferric iron containing 15 grms. per litre, but insoluble in solutions containing less than 10 grms. The ore is so roasted that 25 % of the total copper is present as sulphide compounds insoluble in 5 % nitric acid. A solution containing 30 grms. total iron and 30 grms. copper as sulphates, and about 60 grms. free sulphuric acid, is prepared. This solution circulates between the cells and wet extraction tanks. The cells have lead anodes and no diaphragm. So long as the inflowing solution contains 30 grms. per litre copper, and the effluent 20, the ferric iron will be present in the proper quantity. A portion of the solution is periodically withdrawn and completely precipitated, so that the total iron never exceeds 35 grms. per litre.

A type of mechanical saltcake furnace[23] consists of a pear-shaped pan with screw, which, by reversing, forces the mass into the centre of a roasting furnace in which rotating scrapers move the sulphate to the periphery. A similar endeavour is made by Howard.[24] In this furnace the salt is conveyed to a vessel sealed by salt to a closed mixing chamber and there mixed continuously with vitriol. The material is then conveyed to a single stage mechanical saltcake furnace.

The number of references to the utilization of nitre cake is not as great as the difficulty of disposing of this by-product would suggest. The main reason of this is probably to be found in the lack of time and plant to deal with the large amount now available without restricting the output of more essential products, or requiring materials in demand for these products. Stanes and Rogé[25] suggest heating with sulphur in a non-oxidizing atmosphere, collecting the sulphur dioxide, and converting the acid sodium sulphite to the normal sulphite by further treatment with sulphur dioxide.

A more interesting suggestion from the chemical standpoint is

[22] Eng. Pat. 22745 (1913), *J.*, 1914, 359.
[23] Ch. Fb. Rhenania, Ger. Pat. 279997 (1913), *J.*, 1915, 355.
[24] U.S. Pats. 1145897/8 (1915), *J.*, 1915, 904.
[25] Eng. Pat. 18605 (1914), *J.*, 1915, 961.

represented by the following reactions,[26] regarding the nitre cake solution as sulphuric acid and sulphate—

$$5Na_2SO_4 + 3H_2SO_4 + 6CaSO_3 = 2Na_2SO_4 + 6NaHSO_3 + 6CaSO_4$$
$$2Na_2SO_4 + 6NaHSO_3 + 6CaO = 2Na_2SO_4 + 6NaOH + 6CaSO_3$$

The resulting solution is concentrated, "fished" for the sodium sulphate, and finished for caustic soda.

The use of nitre cake to replace vitriol[27] has been suggested for, and found of use in, the removal of grease from scouring and wool suds, refining grease, stripping colour from rags for shoddy, removal of cotton from mixed fabrics for shoddy, and dyeing rags in the shoddy trade. A solution of 100° Tw. nitre cake with 70 % vitriol has been recommended for the production of sulphate of ammonia.

An ingenious plant, but one which would present great mechanical difficulties in working, is suggested by Basset.[28] Salt is volatilized in a separate furnace and injected into an atmosphere of sulphur dioxide and air. In the absence of water, sodium sulphate and chlorine result; if moisture is present, hydrochloric acid is produced. A more promising alternative is given in which the plant is combined with that required for producing cement from gypsum. A mixture of gypsum, clay, carbon, and salt is introduced into a rotary kiln by a blast of air.

Goldschmidt[29] gives the temperature necessary for the reaction of salt, sulphur dioxide, and air as above 505° C., and suggests the production of chlorine and technically pure salt-cake in an inclined rotary furnace.

Hydrochloric Acid.

The manufacture of hydrochloric acid from magnesium chloride is described by Schwarzenauer[30] and Hepke.[31] According to the former, steam is introduced at the top of retorts containing the magnesium chloride and the acid discharged at the bottom. In Hepke's patent, an infusible mixture of the chloride or oxychloride with magnesia is passed through a rotary kiln heated by direct fire to produce magnesia and hydrochloric acid continuously. Gewerkschaft Amélie[32] endeavour to convert sodium bisulphate into sodium potassium sulphate by

[26] Grossmann, *J.*, 1916, 155.
[27] *J.*, 1916, 109.
[28] Fr. Pat. 477353 (1914), *J.*, 1916, 601.
[29] Eng. Pat. 23287 (1914), *J.*, 1916, 115.
[30] Ger. Pat. 279008 (1914), *J.*, 1915, 227.
[31] Ger. Pat. 278106 (1913), *J.*, 1915, 227.
[32] Ger. Pat. 282253 (1913), *J.*, 1915, 660.

roasting with potassium chloride. The double sulphate is dissolved in water and treated with excess of potassium chloride.

The Soc. Italiana di Elettrochimica[33] describe apparatus for the production of hydrochloric acid by burning hydrogen in chlorine or *vice versa*. The temperature may be moderated by the dilution of the chlorine with an inert gas.

A method of removing arsenic from hydrochloric acid gas is proposed by Friedrich,[34] in which the gas is washed and cooled by sulphuric acid containing hydrochloric acid until this takes up no more arsenic. It is exceedingly doubtful if this suggestion has any practical value.

Nitric Acid.

A good general outline of the production of nitric acid from air, accompanied by descriptions and diagrams of the types of furnaces employed, will be found in the Journal for 1915, p. 113. We propose to deal with the chemical methods in the first place, deferring those which depend upon more physical and engineering problems to a later stage. Raschig[35] describes the production of nitric acid from sodium nitrate and vitriol in a high vacuum at 170°. The supply of the materials and the removal of the residues is effected by vertical pipes of sufficient length to give the requisite head of liquid. The Austrian Verein[36] starts from ammonium nitrate (probably a preparation for the scarcity of sodium nitrate likely to follow the outbreak of war) and decomposes it with at least sufficient vitriol to form ammonium sulphate. Briquetted Chili nitrate with 5 %–10 % vitriol or 10 % ground nitrecake is suggested by Claessen.[37] The concentration of nitric acid is the subject of several patents. Farbw. Meister, Lucius, und Brüning[38] distil low-strength acid (but stronger than acid of minimum vapour pressure) in a still provided with a dephlegmator kept at a suitable temperature by a jacket or by acid vapour from the still. The residual acid of minimum vapour pressure is removed from the still continuously. The Nemours Powder Co.'s patent[39] is similar. According to R. Schall and Stickstoffwerke,[40] a mixture of dilute nitric acid and a dehydrating agent is passed through a tower with a central heating tube. Ribs on the outer wall

[33] Eng. Pat. 24024 (1914), *J.*, 1915, 1142.
[34] *Chem.-Zeit.*, 1916, **40**, 10; *J.*, 1916, 420.
[35] U.S. Pat. 1130104 (1915), *J.*, 1915, 423.
[36] Ger. Pat. 280967 (1914), *J.*, 1915, 491.
[37] Eng. Pat. 6102 (1915), *J.*, 1915, 1009.
[38] Fr. Pat. 472775 (1914), *J.*, 1915, 491.
[39] U.S. Pat. 1149711 (1915), *J.*, 1915, 960.
[40] Ger. Pat. 280965 (1913), *J.*, 1915, 611.

of the tube form a spiral track. A highly concentrated acid is said to be thus produced. The patent of the Norsk Kvaelstofaktieselskab[41] is similar in intention, the nitric acid being treated with a counter-current of vitriol, into which it passes as a mixture of liquid and vapour. Raschig[42] effects the concentration by distillation with concentrated vitriol. The dilute acid is fed automatically and continuously by an air lift to a heated vacuum pan, from which it passes back by gravitation after concentration. After treatment of fifteen parts of 81 % nitric acid with thirty parts of liquid nitrogen peroxide, and allowing to settle after agitation, the patent of Farbw. Meister, Lucius[43] states that the upper layer will contain 98 %–99 % and the lower 75 % acid. The combination of the production of alumina with that of nitric acid is described by the Soc. Anon. des Poudres.[44] Sodium or potassium nitrate is mixed with bauxite and treated with steam at 250°–400° C. The residue is extracted with water to produce alkali aluminate. A cyclic process for the production of ammonium nitrate is described,[45] in which nitrous gases are absorbed in carbonate or bicarbonate solution, the sodium nitrate treated with ammonium chloride. The sodium chloride is finally converted by ammonium carbonate to the sodium carbonate required for the absorption. According to Classen,[46] nitric acid is produced by passing a mixture of nitrogen oxides, oxygen, and ozone (less than 64 % oxygen) over an oxidizing catalyst containing nickel.

The U.S. Commerce Report 176, 1915, gives the output of Chili nitrate for January to March, 1915, as 320,000 tons, with 36 plants in operation against 134 in May, 1914. Shipments to Europe in the second half of 1914 were 651,000 tons, the consumption in the United States being 534,000 tons. The manufacture of sodium nitrate from the calcium salt is stated by Le Chatelier and Bogitch[47] to be commercially impossible below 100° C. owing to the separation of calcium sulphate in the sludge in a slimy form. At 150°–175° C. the sulphate separates easily, enabling a production of 80 % sodium nitrate direct or 93 % when the precipitate is once washed with boiling water.

The problem of the fixation of nitrogen for the production of nitric acid has been very much in evidence for the last few years. The unprecedented demand for nitric acid has given an extraordinary

[41] Eng. Pat. 19792 (1914), *J.*, 1915, 1053.
[42] Ger. Pat. 286973 (1914), *J.*, 1916, 114.
[43] Eng. Pat. 4345 (1915), *J.*, 1916, 537.
[44] Fr. Pat. 473433 (1914), *J.*, 1915, 551.
[45] Eng. Pat. 8270 (1915), *J.*, 1916, 468.
[46] U.S. Pat. 1178440 (1916), *J.*, 1916, 633.
[47] *Comptes rend.*, 1915, 161, 475; *J.*, 1915, 1141.

impetus in this direction and brought about refinements in efficiency and in cost of production which otherwise might have taken years to accomplish. The comparative energy consumption for the different types of plants is given as follows: Birkeland-Eyde, 62; Schoenherr, 59; Frank-Caro, 24; Serpek, 12; Haber, 2. Thus the choice of system is mainly dependent on cheap power or cheap hydrogen.

The power required for the arc process is about five or six times that required for the cyanamide process. The figures given by one writer are for 180,000 tons concentrated acid 540,000 h.p. per annum continuously against 100,000 h.p. for the same quantity by the cyanamide process. The oxidation of ammonia to nitric acid appears to meet with considerable technical difficulties, and certain plants are reported to have experienced a marked falling off in the quality of the products. Schüphaus[48] describes the production of nitric acid from ammonia by passing a mixture of the purified gas and air over platinum gauze at 700° C. A variety of catalysts have been patented, amongst which a number are noteworthy.

The oxidation of ammonia by air is effected by the Verein Chem. Fabr. Mannheim[49] by forcing the mixture through the catalyst so that the pressure of the products is above that of the atmosphere. This may be brought about by a porous plate after the catalyst. Herman[50] burns methane with air enriched with oxygen under high pressure, or causes it to undergo flameless combustion by contact with a mass of zircon. A yield of 3 %–4 % by volume of oxides of nitrogen is claimed with a consumption of about 2·5 cubic metres methane per kilo 100 % nitric acid. The Badische Anilin und Soda Fabr.[51 52] employ a catalyst of the iron group and an oxide of bismuth to oxidize ammonia by air. The claim also covers the replacement of either of the above by an oxide of a rare earth or a mixture of three or more such materials.

The binding material should not contain a large amount of non-metals or their compounds. A yield of 90 % oxides of nitrogen is said to be produced. It is suggested to dissolve fifteen parts of nitrate of iron with one part of lanthanum nitrate in water and precipitate by ammonia. The lumps are dried at 250° C., heated to 600° C., and used at 700° C.

Du Pont[53] claims to produce oxides of nitrogen by successive volumes

[48] *Met. and Chem. Eng.*, 1916, **14**, 425; *J.*, 1916, 621.
[49] Fr. Pat. 492567 (1914), *J.*, 1915, 492.
[50] Ger. Pat. 281084 (1913), *J.*, 1915, 613.
[51] Eng. Pat. 13687 (1914), *J.*, 1915, 961.
[52] Eng. Pat. 13848 (1914), *J.*, 1915, 799.
[53] U.S. Pat. 1147150 (1915), *J.*, 1915, 961.

of air compressed within a long narrow space; each volume of air is allowed to expand under the influence of an arc drawn out between a stationary point and a point moving with the advancing portion of the expanding gas. The gas is heated almost instantaneously to a high temperature and the heat simultaneously converted into mechanical energy.

Fixation of Nitrogen.

The group containing descriptions of methods of the fixation of nitrogen is a large one. The first type with which this synopsis will deal is the combination with hydrogen. This will be followed by the nitride group and the cyanamide group. The Badische Company[54] combine a metal and an activator, one of which absorbs hydrogen and the other nitrogen, thus minimizing the effect of poisons. Reduced iron with 5 % aluminium borate is mentioned as giving a satisfactory yield of ammonia at 500° C. and with aluminium phosphate at 450° C. S. Peacock[55] states that by exposing spongy iron to hydrogen under conditions to form the hydride, and then passing nitrogen (free from oxygen) and hydrogen, ammonia is formed, the hydride being simultaneously reformed.

By passing nitrogen and hydrogen at 100 atmospheres or above over a heated catalyst containing cobalt, sodium, and nitrogen, combination ensues.[56] Other patents claim the use of a catalyst prepared by reducing nickel oxide with hydrogen, adding sodium, and treating the product with ammonia.[57] M. Pier[58] suggests the use of iridium or rhodium with an alkaline or basic contact carrier and the use of magnesia coated with a metal of the platinum group.

Haber and Greenwood[59] describe the action of nitrogen and hydrogen on uranium containing carbon, such as uranium carbonate, at 500° C. under high pressure. Uranium nitride is formed, from which ammonia can be produced by boiling with acids, and from the residue thus left behind a further quantity of ammonia is set free by boiling with alkali.

A process not involving the use of pure gases is described by Bambach.[60] A gas-producer using fuel charged with metallic salts, oxides, or carbides, is the source of the nitrides which are decomposed *in situ*

[54] Ger. Pat. 276133 (1913), *J.*, 1915, 27.
[55] U.S. Pat. 1092167 (1914), *J.*, 1915, 176.
[56] Gen. Chem. Co., U.S. Pat. 1141948 (1915), *J.*, 1915, 799.
[57] Gen. Chem. Co., U.S. Pat. 1143366 (1915), *J.*, 1915, 833.
[58] Eng. Pats. 213 and 214 (1914), *J.*, 1915, 870.
[59] *Z. Elektrochem.*, 1915, **21**, 241; *J.*, 1915, 902.
[60] Fr. Pat. 469331 (1914), *J.*, 1915, 79.

by the water present. The metals can be recovered from the ashes. The gases containing the ammonia are rapidly cooled by a coil in the centre of the furnace. The speed of the reaction is increased by various salts, such as magnesium chloride or calcium fluoride.

According to Dafert and Miklauz,[61] barium nitride is converted to barium hydride and ammonia by heating in hydrogen to about 400° C. At this temperature about 75 % of the nitrogen is converted to ammonia. The nitride is re-formed by heating in nitrogen to 600° C. As an alternative, mixtures and varying temperatures may be used. Another patent[62] is based upon similar reactions, making use of briquettes of lime and carbon. A double nitride is first formed, which is decomposed by hydrogen and nitrogen, yielding calcium nitride and ammonia.

The use of aluminium compounds in ammonia synthesis is based upon the known affinity of aluminium for nitrogen, and use of this property forms the basis of many claims. In one process[63] bauxite, carbon, and iron are heated to produce a material which, after pulverizing, is mixed with sawdust and moistened. Upon exposure to air, spontaneous heating occurs, accompanied by the escape of combustible gases. Impure nitride of aluminium remains behind. When the reaction has started, crude or pure nitrogen is blown into the mass. According to an earlier patent,[64] nitrogen is passed over ferro-aluminium, bauxite, and carbon at 1200°–1300°; the exothermic reaction raises the temperature to 1850°, and maintains it for about five hours above 1500° C.

Two other patents[65] [66] resemble the former process in that alumina mixed with carbon is heated in impure nitrogen (from producer gas), forming a volatile carbo-nitride, from which ammonia is generated by water. The Soc. Gén. des Nitrures,[67] using the same materials, carries them in a stream of nitrogen into an arc furnace, and also uses the "Schwartzkopf" flame for the source of heat in a similar manner.[68] The addition of calcium carbide to ferro-aluminium to fix nitrogen is also suggested.[69] Calcium carbide is also used in White's patent,[70]

[61] Eng. Pat. 16597 (1914), *J.*, 1915, 871.
[62] Peacock and Agric. Research Corpn., U.S. Pat. 1147184 (1915), *J.*, 1915, 961.
[63] Soc. Gén. d. Nitrures, Eng. Pat. 22586 (1914), *J.*, 1915, 353.
[64] Soc. Gén. d. Nitrures, Fr. Pat. 474330 (1913), *J.*, 1915, 1091.
[65] [66] Peacock and Agric. Research Corpn., U.S. Pats. 1154800 and 1154801, *J.*, 1915, 1208.
[67] Fr. Pat. 475908 (1914), *J.*, 1916, 46.
[68] Eng. Pat. 24533 (1914), *J.*, 1915, 423.
[69] Eng. Pat. 4287 (1915), *J.*, 1915, 961.
[70] Eng. Pat. 17937 (1913), *J.*, 1915, 28.

mixed with not less than 25 % of potassium or sodium chlorides or carbonates to fix nitrogen. The resulting cyanamide is pressed and dried or heated in steam to produce ammonia.

Cyanamide, besides its value for fertilizing purposes, is the source of ammonia, cyanides, guanidine, thiourea, and veronal. The world's production of cyanamide in 1914 was about 300,000 tons. Of this the Niagara plant contributed no less than 34,000 tons. At the beginning of the war Germany possessed plant for the production of 50,000 tons of cyanamide; to-day, plant sufficient for 500,000 tons and nearly 10,000 tons arc process nitric acid, built in about eighteen months.

The production of ammonia from cyanamide is embodied in the patents of the American Cyanamid Company,[71] and a fuller description has been given by Landis.[72] An autoclave is charged with 12,000 lb. of water and 7000 lb. of cyanamide and agitated for one hour. Any acetylene thus formed is removed. 2 % Hydrated lime and 3½ % of soda are added. The pressure is raised by steam up to 3 or 4 atmospheres in fifteen minutes, and then the pressure is allowed to rise automatically to 12–14 atmospheres, which is usually the case in about twenty minutes. The ammonia is discharged gradually while maintaining the pressure. After one and a half hours steam is again introduced till 6–8 atmospheres is indicated, when ammonia is again removed. A further steaming may recover a further 2 %. The yield is 98 %. This process is much used in Norway, Germany, France, Switzerland, Italy, and Japan.

To avoid the formation of dicyanodiamide, the addition of less than 6 % of "a salt with an alkaline reaction" is recommended.[73] Other impurities, such as dust, silicon hydride, acetylene, phosphoretted hydrogen, etc., may be removed by washing the ammonia with alkali hydroxide.[74]

The observation that the reaction between calcium carbide and nitrogen takes place readily if the gas is supplied at a pressure corresponding to the dilution of the carbide, has been applied in the production of cyanamide; thus for 60 % carbide, 1 atmosphere; for 50–55 % material, 5–10 atmospheres.[75]

[71] U.S. Pat. 1154640 (1915), *J.*, 1915, 1207.
[72] *Met. and Chem. Eng.*, 1916, **14**, 87; *J.*, 1916, 252.
[73] U.S. Pat. 1149653 (1915), *J.*, 1915, 961.
[74] Oester. Verein, Ger. Pat. 276720 (1913), *J.*, 1915, 28.
[75] Eng. Pat. 3544 (1914,) *C. T. J.*, 1915, 562.

Ammonia.

The manufacture of ammonia by the reduction of nitric acid with hydrogen is nearly quantitative in the presence of finely divided and freshly reduced metals—gold, zinc, and tin being specially active.[76]

The manufacture of carbonate of ammonia by passing ammonia and carbon dioxide into petroleum is suggested.[77] The product, consisting of carbamate, carbonate, and bicarbonate, is filtered off. The Deutsche Continental Gas Gesellschaft describe apparatus for the production of ammonium carbonate, and make suggestions for the use of aluminium or magnalium for this purpose.[78]

The decomposition products obtained by heating alkali ferro- or ferricyanides with exclusion of air are used[79] as the contact substance for ammonia synthesis from its elements. The combination takes place at relatively low pressures and temperatures yielding 17 % by volume of ammonia. Chromium oxide is suggested by the Centralstelle für Wissensch. Untersuch.,[80] as support for the catalyst in ammonia synthesis from its elements. Natural or artificial zeolite, impregnated with platinum chloride, or potassium osmate or ruthenate, dried, heated, reduced by hydrogen, rewashed, treated with ammonium chloride and molybdate or tungsten chloride in acetone, is subject of an additional patent of the Badische Co.[81] Thorssell[82] obtains ammonia from barium cyanide by agitation with water followed by heating under 15 atmospheres to produce barium formate and ammonia.

With regard to the production of ammonia by the older methods a few notices occur. The quantity of the ammonia from all sources manufactured in Great Britain is given as 432,000 tons in 1913 and 421,000 tons in 1914 calculated as sulphate. Of this quantity gas works contributed 173,000, iron works 16,000, shale distillation 58,000, coke ovens 176,000 tons.

A description of the Striebeck system, or modification of the ammonia soda process, is given by Jurisch.[83] The apparatus consists of a tower ten yards high (which can be made in a single casting), divided into compartments by horizontal steps. Low steam consumption is claimed, but the short life of the tower and cleaning difficulties militate

[76] Adhikary, *Chem. News*, 1915, **112**, 163 ; *J.*, 1915, 1053.
[77] Badische Fabrik, Eng. Pat. 8763 (1915), *J.*, 1915, 904.
[78] Ger. Pats. 285498, 285531, and 286241 (1914), *J.*, 1915, 1143, 1249.
[79] Bayer & Co., Ger. Pat. 285698 (1914), *J.*, 1915, 1143.
[80] Ger. Pat. 288496 (1914), *J.*, 1916, 360.
[81] Eng. Pat. 1358 (1915), *J.*, 1916, 689.
[82] Eng. Pat. 11485 (1915), *J.*, 1915, 1207.
[83] *Chem. Ind.*, 1915, **38**, 9, 61 ; *J.*, 1915, 1246.

against its adoption. Thelen calciners and the Honigmann form of ammonium chloride liquor decomposers are used.

A reference which should stimulate English producers of ammonium sulphate contains the statement, which unfortunately is true in most cases, that the German product is a better product, both in regard to the mechanical condition and freedom from corrosive action on the bags.

The process of Collett and Eckhardt[84] possesses some points of interest. Ammonia gas is passed into a mixture of sulphur dioxide, air and moisture producing $(NH_4)_3\,H(SO_4)_2$, which is further oxidized to the normal sulphate in a system of towers on the countercurrent system.

Owing to the demand for vitriol the manufacture of ammonium sulphate in Germany is replaced by the manufacture of concentrated liquor by distilling off into a special type of distillation columns, producing liquor practically free from carbonate.

An automatic still, with heat interchangers, for the production of 26 % liquor from 1 % is described by Knoedler.[85]

A suggestion for the direct production of ammonium chloride in gas works is made by Strommenger.[86] The liquors are treated with hydrochloric acid in excess and blown with air. The sulphur is separated and ammonia is then added to remove the iron. The filtrate is neutralized with hydrochloric acid, salt added, and the solution evaporated. The crude muriate is sublimed and recrystallized.

The Badische Co.[87] propose the treatment of an alkali chloride, in presence of water, with vitriol and ammonia. The alkali sulphate is separated and the muriate crystallized from the mother liquor.

The troublesome effect of arsenic in the manufacture of sulphate of ammonia is dealt with by Parrish.[88] According to circumstances the removal of the arsenic may be carried out by (*a*) oils, as in the shale industry; (*b*) the use of a closed saturator with skimming; (*c*) precipitation of the arsenic as sulphide by the waste gases from the saturator.

Cyanides.

The conversion of cyanamide into cyanide free from sulphide is brought about by heating for 20 minutes to 800–1000° C. with an equal weight of a mixture containing 50 % sodium sulphide and 50 %

[84] Eng. Pat. 16629 (1911), *J.*, 1912, 640.
[85] *J. Ind. Eng. Chem.*, **7**, 1061; *J.*, 1916, 111.
[86] *Z. angew. Chem.*, 1914, **27**, 518; *J.*, 1915, 17.
[87] Ger. Pat. 290747 (1914), *J.*, 1916, 601.
[88] *J. Gas Lighting*, 1916, **134**, 134; *J.*, 1916, 535.

chloride. Some interest may be aroused as to the purpose of A. Lang, whose patent is here summarized.[89] A mixture such as 1 part aluminium, 2 iron, 5 barium nitrate, and 0·8 ammonium oxalate on decomposition, brought about by the heat of reaction of the first three components, forms hydrocyanic acid. Another mixture enclosed in a cartridge, with metallic cover, liberates cyanogen, "especially if oxygen is restricted as in caves, etc."

Production of Hydrogen.

The production of hydrogen is intimately connected with the manufacture of synthetic ammonia and has been the subject of a large group of patents and descriptive articles. The chief types may be summarized as follows:—

(1) Linde-Frank-Caro process, from water gas by liquefaction and fractionation.
(2) Decomposition of water by iron.
(3) Decomposition of hydrocarbons at a high temperature by coke, and purification of the products by bog iron ore, etc., and removal of carbon monoxide by soda lime at about 300° C.
(4) Electrolysis of dilute caustic soda with the simultaneous production of oxygen.

Military necessities have brought into notice other methods, the importance of portable apparatus outweighing other considerations. The use of both silicon and ferro-silicon is also suggested. The alleged comparative costs of the various methods per cubic metre are as follows: Silicon and caustic 4*s.* 5*d.*; "Hydrolith" 4*s.* 2*d.*; "Hydrogenit" 1*s.* 4*d.*; iron and acid 1*s.* 0½*d.*; water gas 1*s.* 0*d.*; ferrosilicon 10*d.*; oil gas 1¾*d.*; water and iron 1½*d.*

A variety of catalytic agents have been announced. Of those utilizing water gas the following are probably the most important. Buchanan and Maxted[90] use the ferrite compound produced by roasting pyrites cinders with soda ash, after the recovery of the caustic soda. The Badische Co.[91] claim a practically quantitative yield at a temperature of 600° C. by the use of activating compounds. The oxygen compounds of chromium, thorium, uranium, beryllium, antimony, and the like are mentioned in this connection; the presence of nickel is claimed as hindering the formation of methane. Other agents such as an iron-copper or iron-silver couple have been suggested,

[89] Ger. Pat. 287006 (1914), *J.*, 1916, 176.
[90] Eng. Pat. 6476 (1914), *J.*, 1915, 177.
[91] Ger. Pat. 279582 (1913), *J.*, 1915, 355.

and other variations of procedure described. The action of metals on water under pressure is made use of by Bergius[92] and others[93]; as the methods of production are mechanical, further detail is not required. Linde-Claude types of machine, capable of producing more than 30,000 gals. per hour, are already installed. The product is mainly for fractionation. Neon, as a by-product, is employed for electric bulbs. The oxygen is used for welding and cutting metals and for enriching blast furnace blast. The chief uses of the nitrogen have already been given.

Magnesium.

The manufacture of magnesia from dolomite is described in a patent of J. A. Bradburn,[94] by calcination at 900° C. and treatment of the solution produced by lixiviation by sodium and ammonium chlorides. The ammonia is recovered and magnesium hydroxide precipitated by calcined dolomite.

Lime Salts.

The method of working up lime sludge (from causticisers or sugar refining) by calcination in a rotary kiln is described by Meade.[95] The accumulation of impurities is avoided by the addition of 5–10 % fresh lime. It has been stated[96] that a plant for the recovery of lime from causticiser mud by this method has run effectively for more than a year. Recovered calcium sulphate,[97] by treatment at a suitable temperature with sodium and magnesium carbonates in the presence of sodium or potassium chloride as catalyst, is converted into magnesium sulphate and calcium carbonate.

Hydrosulphites.

Hydrosulphite of soda, under the name of "Blankit," is much used in the sugar industry. The proposal has been made to produce this salt in the factory, no chemist being necessary. A burner producing sulphur dioxide free from oxygen is required. The zinc salt is first produced and converted into the sodium salt by caustic soda. The Badische patent[98] describes a continuous electrolytic process, the bisulphite liquor being circulated through cells and enriched with

[92] Ger. Pat. 277501 (1913), *J.*, 1916, 229.
[93] Näher and Nöding, Ger. Pat. 286960 (1914), *J.*, 1916, 177.
[94] U.S. Pat. 1156662 (1915), *J.*, 1916, 254.
[95] *Met. and Chem. Eng.*, 1915, **13**, 289; *J.*, 1915, 608.
[96] *Jour. Ind. Eng. Chem.*, 1915, **7**, 1056; *J.*, 1916, 110.
[97] Jacob, Fr. Pat. 474509 (1913), *J.*, 1915, 1091.
[98] Ger. Pat. 278588 (1912), *J.*, 1915, 229.

sulphur dioxide until the salt crystallizes out. The difficulty in the removal of the last traces of water is overcome[99] by heating at 60–65° C. in the presence of aniline or other equivalent base. The removal of water can also be effected by treating the sodium or sodium-zinc salt with sodium acetate in alcohol.[100]

Potash Salts.

The references to the extraction of potash salts from raw materials of non-German sources are very numerous, consequently an endeavour will be made to indicate only the general tendency of the work devoted to the subject. The value of the sales of the German Syndicate is given as £78,000,000 in 1914, compared with £96,000,000 in 1913.[101] The quantity of crude salts mined amounted to 11,607,510 metric tons from about two hundred mines. The Chili deposits[102] contain over 2,000,000 tons of muriate. Some samples gave KCl 14·15, NaCl 51·45, Na_2SO_4 29·39 %.

Old village sites in India can produce about 15,000 tons of saltpetre per annum by lixiviation of the soil. The writer of these notes has seen in old churchwardens' accounts the payment of sums of money to saltpetre men to keep out of the churchyards. There was a shortage of munitions during the Civil Wars, and it appears that the salts of such soils could be made use of to mitigate the shortage of powder. Other sources are twenty-four factories in the Caucasus, where sunflower stalks are worked up for potash. In passing, we may add that the ash from weeds, hedge clippings, vegetable refuse, and notably banana stalks, yield an ash containing 15 % or more of K_2O. The extraction from sugar residues and wool scouring is likely to prove of value as a side issue to those industries. Some of the American felspars have a high potash content, about 18 % K_2O at Kingston, and rather higher down the St. Lawrence. The British felspars are usually rather poor, but occur in large masses in Mull, Mourne Mountains, Lanlivery, St. Barule, Lundy, Rubislaw, and Cove. A good summary of the possible mineral sources of potash is given by Cresswell.[103] One report[104] estimates the Spanish (Santander and Cardona) deposits to contain 2,550,000 tons of carnallite, and 1,150,000 of sylvine. At Cardona there are 70 ft. of carnallite with 20 % muriate, and 33 ft. of sylvine with 95 % muriate. Searles Lake in California is reported to

[99] Chem. Fabr. Griesheim-Elektron, Ger. Pat. 279389 (1913), *J.*, 1915, 355.
[100] Kinzlberger, Ger. Pat. 280181 (1912), *J.*, 1915, 355.
[101] *Board of Trade J.*, Feb. 11, 1915; *J.*, 1915, 175.
[102] *Eng. and Min. J.*, 1915, **100**, 218.
[103] *J.*, 1915, 887.
[104] *U.S. Comm. Rept.*, July, 1915; *J.*, 1915, 869.

contain 6,000,000 tons of muriate. The chief difficulty in exploiting these deposits is that due to transport. The production of potash products from felspars has proved a difficult problem, and it seems likely that it will not prove remunerative in normal times unless combined with the production of other materials of definite market value and in considerable demand. A rotary kiln with an annual capacity of 4000 metric tons of clinker would produce 1600 metric tons K_2O from the volatilized salts.[105] In 1915, potassium muriate recovered in cement manufacture was valued at $342,000, and the dust nuisance was very much reduced.

The felspar is strongly heated in a rotary kiln with lime. Other materials are added, such as calcium or sodium chloride, if a muriate is desired. In this manner, by lixiviation and concentration, a product containing 70–80 % muriate and 14–16 % salt has been produced. By the addition of gypsum to the felspar before calcination, or by lixiviation with vitriol afterwards, sulphates and alums can be obtained. The use of barium sulphate has also been proposed. The fine dust in this case may contain as much as 94 % sulphate of potash and some carbonate. The calcination of felspar with nitre cake and carbon, especially mine "tailings," if rich in potash-bearing rocks, might yield a marketable product at a reasonably low cost in certain circumstances. Pichard[106] claims a theoretical yield of potassium nitrate from the action of sodium nitrate on potassium chloride by the addition, during cooling to 0° to 3° C., of anhydrous sodium sulphate, rendering the saltpetre insoluble and withdrawing water. Another method of extracting[107] the saltpetre from salts containing potassium muriate employs a salt solution containing enough sodium nitrate to convert the potash to nitrate. By concentration the potassium nitrate and some salt crystallize out, and by a careful leaching the nitrate is separated.

The question of the utilization of seaweeds has also been the source of many attempts to produce potash salts. Cameron[108] estimates that the available beds of the Pacific coast could yield 2,266,000 tons of muriate from kelps containing 9–20 % K_2O and trace—1·9 %, of iodine. Klingbiel[109] suggests treating the lixiviation liquor from kelp ashes with phosphoric acid rendered neutral with an alkali. By this means the separation can be carried much further than has hitherto been possible, and a mother liquor rich in iodine obtained. Another

[105] *Chem.-Zeit.*, 1915, **39**, Rep. 63; *J.*, 1915, 421.
[106] Fr. Pat. 471237 (1913), *J.*, 1915, 176.
[107] Pichard, Fr. Pat. 472503 (1913), *J.*, 1915, 492.
[108] *U.S. Comm. Rept.*, June 19, 1915; *J.*, 1915, 869.
[109] Ger. Pat. 277109 (1913), *J.*, 1915, 138.

method starts with the pulping of the kelps, freeing from air by reduced pressure, heating to 170° C. to destroy the slime constituents, and pressing; the liquid thus obtained contains about 70 % of the original alkali, 90 % of the iodine, and 33 % of the nitrogen. The dried cake is incinerated or burnt in a producer to recover the nitrogen and the ash extracted for alkali. In another process[110] the kelp is pressed, the liquor acidified with vitriol, and the algin filtered off. Calcium carbonate is then added till neutral and some soda. The press cake is pulped and boiled with the solution thus obtained to separate the cellulose, algin is precipitated with acid, and after neutralizing is evaporated. A different method of attack is to ferment the seaweed with *Oidium lactis* and *Aspergillus glaucus*, wash with alkaline liquid, and recover the salts in the known manner.

The loss of iodine during the incineration of kelp, even when the temperature is kept low, is avoided by extracting at a temperature of about 150° C. under pressure. Zoller[111] shows that the salts can be extracted from wood waste by water at 80°–90° C., Douglas fir yielding about 3½ % potash with much sodium chloride.

The extraction of iodine may be accomplished by electrolysis, electrodes of lead being used.[112]

Bromine production has again been taken up in Ohio and Mason City from wells which have been long idle. The Michigan and Pennsylvania salt industries have also contributed. The total output 1905–1907, 642 tons; 1910, 122 tons; 1911–1914, 306 tons.

Aluminium Compounds.

Patents relating to the production of alumina and aluminium salts have been rather numerous, but do not reveal much of a novel character. In one process[113] aluminous material is treated with sulphurous acid, and by careful heating and agitation the alumina and silica are successively precipitated. Another method of effecting the separation is suggested[114] in which the bauxite, or clay, is heated so as to reduce the alumina, but not the silica. The iron is removed by heating in chlorine below 500° C., followed by the chlorination of the aluminium at 900° C.

[110] Kelp Products Co., U.S. Pat. 1136390 (1915), *J.*, 1915, 612.

[111] *J. Ind. Eng. Chem.*, 1916, **8**, 105; *J.*, 1916, 466.

[112] Pisarshevski and Tjelmi, *J. Russ. Phys. Chem. Soc.*, 1915, **47**, 2060; *J.*, 1916, 421.

[113] Exolon Co., U.S. Pat. 1148092 (1915), *J.*, 1915, 905.

[114] Virginia Lab. Co., U.S. Pat. 1147832 (1915), *J.*, 1915, 905.

The Bayer process is one of great interest, and the principles involved are almost certainly applicable to other problems of a similar character. In this process aluminates are agitated with aluminium hydroxide, which causes the precipitation of alumina. Hirsch and Russ[115] suggest the use of ozonized air to decolorize the solution and produce a white alumina. Martin[116] proposes to calcine aluminous earths with limestone at 1300° C. and wash in two stages with soda at 80° C., yielding aluminates free from silica. The auto-precipitation is then carried out by the Bayer process. The process of Spence and others[117] deals with the working up of the impure solutions obtained from shales by treatment with bauxite, alumina-silicate, or basic aluminium compounds. The excess of potash is removed as alum, the liquid heated to a temperature of 55°, or up to the boiling point according to the specific gravity. Bauxite is then added to obtain neutral aluminium sulphate, and contact kept up until the iron is removed. In general a temperature higher than 55° and a specific gravity higher than 1·3 is best for the solution of alumina and removal of the iron, but higher specific gravities and lower temperatures are advantageous in preventing the precipitation of basic insoluble compounds.

Graphite.

Two references to graphite possess points of interest, as they afford examples of the rapidly increasing importance of the practical application of colloidal chemistry. Plauson[118] proposes to treat coke powder (purified with mineral acids) with natural colloids or aldehydes, tannin, tungstic acid, or chromic acid to produce graphite in colloidal form. The Acheson Co.[119] produce deflocculated graphite by treatment with tannin. The paste is stirred with water and treated with acetone, ethyl or methyl alcohol. The precipitated material is then dried and is at once deflocculated on treatment with water. Lampblack and the like, after the treatment outlined above, may be pressed into sods or other convenient forms.

Formic, Acetic, Lactic Acids, etc.

A few references, mostly of considerable theoretical interest and likely to yield valuable practical results in the future, are found in the period covered by this synopsis.

[115] Ger. Pat. 284601 (1912), *J.*, 1915, 1091.
[116] Eng. Pat. 9662 (1915), *J.*, 1916, 46.
[117] Eng. Pat. 2048 (1915), *J.*, 1916, 422.
[118] Eng. Pats. 17731 and 17732 (1913), *J.*, 1915, 799.
[119] U.S. Pat. 1116957 (1914), *J.*, 1915, 228.

Bredig and Carter[120] give equilibrium observations made upon the method of producing formic acid from carbon dioxide by the action of hydrogen and palladium black in the presence of water. Between 30° and 90° C. no formation of formic acid was noted, and consequently it appears unlikely that formic acid forms a stage in the assimilation of carbonic acid in nature. The results of these observations are embodied in patents.[121] Formates are produced by the action of compressed hydrogen upon bicarbonates in the presence of catalysts. A 75 % yield of potassium formate is obtained by passing hydrogen at 60 atmospheres pressure vigorously through 200 c.c. of a 5 % solution of potassium bicarbonate containing 1·5 g. of palladium black, a 20 % yield by passing similarly carbon dioxide and hydrogen at 20 atmospheres into a 5 % borax solution in the presence of the same catalyst.

Haakh[122] combines the production of ammonia with that of formates by the following reactions:—

$$K_4Fe(CN)_6 + 14H_2O = 4HCOOK + 2HCOONH_4 + 4NH_3 + Fe(OH)_2$$

If potash be used, a pure solution of potassium formate is obtained after separating the precipitated iron and distilling off the ammonia.

The production of acetic acid from acetylene, as suggested by the Chem. Fabr. Griesheim-Elektron,[123] is likely to prove of practical interest in the near future. By the interaction of acetylene, oxygen and water in the presence of mercury compounds, acetic acid is readily synthesized. The reaction is carried out in an acetic solution (or chloracetic or lactic). Accelerators such as iron or vanadium oxides, phosphoric or sulphuric acids and bisulphates may be used (see page 271).

Galitzenstein[124] claims to obtain glacial acetic acid from low-strength acetic acid by extracting with solvents such as chloroform, benzene petroleum ether, or sym. dichlor-ethylene, and removing the solvent by distillation.

Haupt[125] proposes to obtain sodium oxalate by atomizing molten sodium by an injector operated by heated carbon dioxide. The yield is claimed to be quantitative. Portheim[126] introduces a catalyst in the production of oxalic acid from carbohydrates and nitric acid, the oxides of nitrogen being recovered for use again in the process.

[120] *Chem.-Zeit.*, 1915, **39**, 72; *J.*, 1915, 278.
[121] Bredig and Carter, Eng. Pats. 801 and 9762 (1915), *J.*, 1915, 1143, 1207.
[122] Ger. Pat. 281044 (1913), *J.*, 1915, 611.
[123] Fr. Pat. 473158 (1914), *J.*, 1915, 491.
[124] *Z. angew. Chem.*, 1916, **29**, 148; *J.*, 1916, 535.
[125] Ger. Pat. 286461 (1913), *J.*, 1915, 1144.
[126] U.S. Pat. 1157348 (1915), *J.*, 1915, 1207.

Landau[127] obtains a pure lactic acid by decolorizing commercial acid with animal charcoal in a vessel fitted with a reflux condenser, a current of inert gas being passed through continuously. The liquid is then concentrated up to 90 % to 95 % by distilling off the water, preferably *in vacuo*. Dextrin or other organic matter is precipitated by the addition of one and a half times its weight of alcohol. After settlement and filtration, the alcohol is removed by distillation.

Argon and Neon.

Argon, according to Washburn,[128] is now manufactured in large quantities for electric bulbs by passing nitrogen through cyanamide furnaces until a concentrated argon remains.

In another process[129] oxygen rich in argon is passed together with hydrogen over heated copper. The method is simplified by burning oxygen and hydrogen in the theoretical proportions in closed cylinders, the walls of which are kept cool. A further purification is effected by heated copper.

Neon obtained in the fractionation of liquid air is also employed in the filling of electric bulbs.[130]

Radium, etc.

The industrial uses of radium emanation are given by Baker,[131] and include the following observations. The growth of mustard seed is promoted by the α-rays; the β and γ are injurious. Germination is adversely affected by uranium, and consequently radium ores should be freed from this element before use. For external medical use, radium-barium sulphate should be fused with sodium chloride and the aqueous solution of the product employed. Photographic emulsions give denser results when radium chloride or bromide is incorporated in them. The bactericidal action of radium may also be of practical use in the fermentation industries.

A good summary of the sources of radium and the methods of extraction is given by Ebler and Bender.[132] A report presented to the House of Representatives[133] and another by the Bureau of Mines[134] afford further details. The most extensive radium-bearing deposits appear to

[127] Eng. Pat. 7998 (1915), *J.*, 1915, 1009.
[128] *Chem. News*, 1915, **112**, 29; *J.*, 1915, 796.
[129] Griesheim-Elektron, Fr. Pat. 473985 (1914), *J.*, 1915, 717.
[130] *Engineering*, 1915, **99**, 98 and 155; *J.*, 1915, 282.
[131] *J. Roy. Soc. Arts*, 1915, **63**, 490; *J.*, 1915, 490.
[132] *Z. angew. Chem.*, 1915, **28**, 25; *J.*, 1915, 279.
[133] *Chem. News*, 1914, **110**, 264, etc.; *J.*, 1915, 77.
[134] *U.S. Comm. Rept.*, July 27, 1915; *J.*, 1915, 870.

be the carnotite ores in Colorado and Utah. Much of the ore which was formerly wasted is now recovered owing to the enhanced efficiency of modern methods. Up to July, 1915, 3 grammes of radium in the form of radium-barium sulphate, containing over 1 milligramme per kilogramme of sulphates, had been produced. Bredt[135] describes a method of extraction by fusion of the sulphate residues with enough soda to convert 95 % into a soluble form ; the insoluble portion containing the radium is separated, and the operation repeated until the desired concentration is reached. An alternative method consists in boiling with concentrated sulphuric acid, and the radium precipitate which forms on cooling is collected. Ebler and Bender[136] employ calcium carbide to reduce the mixed sulphates, and are able to reduce the quantity of calcium hydride, which was formerly used[137] in the autogenous reduction. A commercial method for the separation of vanadium and uranium from carnotite is described by Plum,[138] whereby 90 % radium, 50 % polonium, 52 % actinium, and 61 % ionium present can be extracted and separated. Further work on the extraction of radium has been carried out by Parsons and others,[139] who dissolve the radium from the carnotite with hot concentrated nitric acid, and, after removal of the admixed elements, reduce the crude sulphates with carbon. The crude sulphides are treated with hydrochloric acid and the chlorides crystallized out in silica vessels. The procedure, which is described in detail, is apparently an efficient one.

Lind[140] gives a full account of the electroscopic method of determining the radium content of products containing that element. For some time very considerable difficulties in reconciling the analytical data of different observers have been noted, but the standardization of methods is now being rapidly established. Thorium X is obtained by Lorenzen[141] by dialysing colloidal thorium oxide, the thorium X passing through the membrane. The thorium X is continuously generated from the radio-thorium, and consequently more passes through when the dialyser is refilled with distilled water. Jost and Weinert[142] suggest the recovery of thorium as the pyrophosphate, owing to the very small solubility in dilute acids. Radio-thorium,

[135] U.S. Pats. 1154230 and 1154231 (1915), *J.*, 1915, 1143.
[136] *Z. anorg. Chem.*, 1914, **88**, 255 ; *J.*, 1915, 78.
[137] *J.*, 1913, 976.
[138] *J. Amer. Chem. Soc.*, 1915, **37**, 1797 ; *J.*, 1915, 959.
[139] *U.S. Bureau of Mines*, Bull. 104 ; *J.*, 1916, 44.
[140] *J. Ind. Eng. Chem.*, 1915, **7**, 406 ; *J.*, 1915, 610.
[141] Ger. Pat. 278121 (1913), *J.*, 1915, 228.
[142] Ger. Pat. 286087 (1914), *J.*, 1915, 1144.

according to Kuhnheim and Co.,[143] is separable from neutral solution containing small quantities of rare earths by treatment with hydrogen peroxide. The radio-thorium peroxide can be filtered off, and the thorium X can be removed by extraction with dilute salt solution. Investigations into the adsorption of radium elements have been carried out by Horovitz and Paneth,[144] with interesting results.

The separation of rare earths by the fractional crystallization of the nitrobenzene sulphonates (Holmberg's proposal) has been satisfactorily applied by Garnier[145] to didymium-samarium mixtures. Siemens and Co.[146] describe the production and separation of rare earths by means of the double fluorides. The yields claimed approach very nearly to the theoretical.

A full account of the sources and industrial uses of beryllium compounds[147] is of interest. The beryllium compounds, which are used to give increased strength to gas mantles, prior to the war were manufactured in Germany, but British products for this purpose are now on the market.

References to other articles which do not easily permit of short summaries, but which may with advantage be read by those desirous of a general survey, are added here:—

"Exports of Heavy Chemicals from Germany," *J.*, 1915, 136.
"The Chemical Industries of Germany," *J.*, 1915, 307.
"Effect of War on British Chemical Industry," *J.*, 1915, 327–340.
"Retrospect of Indian Chemical Industry," *J.*, 1915, 420.
"Chemical Reactions at Low Pressures," *J.*, 1215, 490.
"The Disposal of Nitre Cake," *J.*, 1915, 1121.
"Technical and Academic Chemistry," *J.*, 1915, 1122.
Proceedings of the Annual Meeting, *J.*, 1915, 745.

[143] Kuhnheim & Co., Ger. Pat. 279956 (1913), *J.*, 1915, 355.
[144] *Chem.-Zeit.*, 1914, **38**, 1206; 1915, **39**, 25; *J.*, 1915, 281, 423.
[145] *Arch. Sci. Phys. Nat.*, 1915, **40**, 93, 199; *J.*, 1915, 1248.
[146] Eng. Pat. 9087 (1914), *J.*, 1915, 871.
[147] *Bull. Imp. Inst.*, 1914, **12**, 613; *J.*, 1915, 352.

GLASS AND CERAMICS.

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Glass Research.

The outstanding feature in connection with the glass industry since the commencement of the war is the commercial production of types of glass previously supplied exclusively from enemy countries. The sudden and complete cessation of supplies proved to be a strong stimulus, and many of the necessities of the situation have been adequately met in a surprisingly short space of time—a gratifying state of affairs only rendered possible by the results of scientific research. In February, 1915, "Notes on Glass"[1] were issued from the National Physical Laboratory, giving analyses of thermometer and chemical glassware, and of lamp glasses, with some other data. This was soon followed by the valuable first report of the Glass Research Committee appointed in October, 1914, by the Institute of Chemistry.[2] This Committee consisted of the late Prof. R. Meldola (then President of the Institute), Prof. Herbert Jackson, and Messrs. B. Blount, O. Hehner, W. C. Hancock, and T. R. Merton. Their chief objects were to provide working formulas for all laboratory glassware, and to investigate the influence of different ingredients on the chemical and physical properties. Miners' lamp glasses and glass for ampoules used by wholesale pharmaceutical chemists were also included in the scope of the researches. The work of the Committee was greatly facilitated by the fact that Prof. Jackson and Mr. Merton at King's College, London (and Prof. Jackson also at his private laboratory), had already made substantial progress with work of a similar nature undertaken independently. Prof. Jackson and Mr. Merton continued their investigations under the auspices of the Committee, the other members assisting materially by contributing analyses of various glasses. The results obtained were placed at the disposal of the Committee, and the first report communicated eleven formulas for glasses of the types indicated, based on the results, tested as thoroughly as possible on a small scale,

[1] *J.*, 1915, 210. [2] *Proc. Inst. Chem.*, 1915, Part 2, 33; *J.*, 1915, 424.

of about 400 experimental melts. Of these two were for miners' lamp glasses, four for soft glasses, three for glasses for combustion tubing, and two for resistance glasses. The formula for a very soft glass,[3] suitable for sealing platinum into soft glass and for joining to soft glass tubing, was next published. In a subsequent report[4] two additional formulas are given, in which the use of the comparatively expensive alumina is avoided, for soft glasses corresponding to Nos. 1 and 11 of the first series. The Committee continued the experiments aided by grants from the Advisory Council on Scientific and Industrial Research, and have since reported 19 other formulas for special glasses,[5] including opal glass, glasses for electric light bulbs and thermometers, optical glasses, etc. These have not been published, but have been communicated to British manufacturing firms. The Advisory Council has also recommended Government grants in aid of new researches on optical glass by Dr. W. Rosenhain, F.R.S., at the National Physical Laboratory, and on glass technology by the Sheffield University Delegacy at the Research Institute attached to the University of Sheffield.

F. W. Branson[6] independently investigated the composition of chemical glassware and miners' lamp glasses, and several varieties based on results of his researches have been manufactured on a commercial scale.

Opalescence of Glass.

The causes of the opalescence of glass are discussed by J. G. Smull,[7] who concludes from results of his own investigations that the opacity is due to separation of either silica or alumina, or both, in a very finely divided, probably colloidal, form in the glass, the most suitable condition for this separation being a lead glass (having, of course, a low melting point), where the silica and alumina will remain suspended for some time before going into solution. The separation of silica and alumina is effected (*a*) by the use of silicates, such as felspar, in conjunction with a fluoride; (*b*) by a double fluoride, such as cryolite, with or without felspar; (*c*) by silicofluorides, with or without felspar; (*d*) by a fusion of the major ingredients of a glass, with the subsequent addition of a fluoride and other desired substances to the fused portion. The separated material has different refractive power from that of the glass medium.

[3] *Proc. Inst. Chem.*, 1915, Part 3; *J.*, 1915, 962.
[4] *Ibid.*, 1915, Part 4, 6; *J.*, 1916, 116.
[5] *Ibid.*, 1916, Part 3, 7.
[6] *J.*, 1915, 471.
[7] *J.*, 1915, 402.

Oxidizing and Decolorizing Agents for Glass.

S. R. Scholes[8] has demonstrated experimentally the correctness of the view of Dralle and Hovestadt in ascribing the violet tint imparted to glass by addition of manganese dioxide (serving effectively to mask the green colour produced by iron) to manganic oxide, Mn_2O_3. In another article[9] the same author suggests that during annealing a part of the manganese in the glass takes up more oxygen to form green manganate.

Since the war commenced, the extraordinary demand for nitrates in connection with the manufacture of explosives has stimulated a keen search for efficient substitutes to replace the nitrates of potassium and sodium used in making glass, and the Germans have been very active in this direction.

L. Springer[10] reports that experiments on a working scale have shown that in the glass industry potassium nitrate may be replaced by potassium chlorate or perchlorate, but owing to the volatility of potassium chloride an addition of sodium or potassium carbonate is also necesssary to maintain the desired viscosity. Sodium chlorate has also been suggested,[11] and other proposed substitutes for potassium nitrate include peroxides (of sodium and barium), sodium perborate, and persulphates, though some of these would probably be too costly for use on a commercial scale. As decolorizing material for glass L. Springer also refers to antimony oxide,[12] and elsewhere he discusses the substitution of potassium permanganate[13] for potassium nitrate, recommending it as suitable, subject to satisfactory practical tests on a large scale. In another article L. Springer asserts the feasibility of employing barium peroxide[14] instead of potassium nitrate. Reference is also made by Springer[15] to a preparation (the composition of which is not disclosed) patented by Schott and Co., of Jena, which changes the bluish-green colour of the glass to a light yellowish of considerably less strength, while the gas bubbles are at the same time removed from the glass. The oxygen is also first evolved at a higher temperature than with other oxidizing agents. When no sodium sulphate is used, the preparation can be added directly, 0·5 % being usually sufficient, and addition of potassium nitrate or arsenic is superfluous. For the purpose of oxidizing glasses which are melted with sodium sulphate, the preparation is introduced in the form of solid pieces, like arsenic is

[8] *J. Ind. Eng. Chem.*, 1915, **7**, 1037; *J.*, 1916, 116. [9] *J.*, 1916, 518.
[10] *Sprechsaal*, 1916, **49**, 96, 104; *Z. angew. Chem.*, 1916, **29**, Ref., 304; *J.*, 1916, 840. [11] *Ibid.*, 1915, **48**, 41.
[12] *Ibid.*, 1915, **48**, 97, 106, 211, 221.
[13] *Keramische Rundschau*, 1915, **23**, 214; *Sprechsaal*, 1916, **49**, 167.
[14] *Sprechsaal*, 1916, **49**, 136, 144. [15] *Ibid.*, 1916, **49**, 167.

added in many glassworks; to complete the decolorization, a small amount of manganese or similarly acting colouring material is added in this case.

Glass Furnaces.

In a novel method used at Bunzlau for heating glass-smelting furnaces,[16] the furnace is provided with means for regulating independently the heat supplied to each melting pot or group of melting pots, and the waste gases from the heating of each pot or group of pots are passed to a regenerator or recuperator corresponding to such group. Refractory glass and soft glass can thus be melted in different pots in the same furnace, and a defective pot may be cooled enough to allow of its replacement without interfering with the working of the rest of the furnace. The same principle may be applied to tank furnaces with several tanks.

Other patents for glass furnaces of various types can only be very briefly alluded to. New or modified tank furnaces have been invented by G. E. Howard,[17] L. Steelman,[18] R. H. Bolin,[19] O. Gobbe,[20] and G. W. Batchell.[21] Regenerative glass furnaces have been patented by W. N. Matthews,[22] W. L. Monro,[23] C. Menzel,[24] and T. W. Connington[25] The glass furnace patented by S. B. Bowman[26] has a mechanical arrangement for detaching definite amounts of molten glass. Most of these inventions are American.

Special Methods of Manufacture.

In the manufacture of continuous glass sheets by the method of drawing from a mass of molten glass, H. T. E. Kirkpatrick[27] adopts special means for regulation of the currents of air.

R. G. Kann[28] claims to ensure regular results by mixing the ingredients in small quantities, making into briquettes, and supplying a

[16] Ger. Pat. 287159, 1913, *J.*, 1916, 178.
[17] U.S. Pats. 1138110 and 1138111, 1915, *J.*, 1915, 641.
[18] U.S. Pat. 1145815, 1915, *J.*, 1915, 906.
[19] U.S. Pats. 1163584 and 1163585, 1915, *J.*, 1916, 116, 117.
[20] Ger. Pat. 288778, 1913, *J.*, 1916, 424.
[21] U.S. Pat. 1181283, 1916, *J.*, 1916, 691.
[22] U.S. Pat. 1152828, 1915, *J.*, 1915, 1055.
[23] U.S. Pat. 1157246, 1915, *J.*, 1915, 1209.
[24] Ger. Pat. 289827, 1915, *J.*, 1916, 424.
[25] U.S. Pat. 1172674, 1916, *J.*, 1916, 469.
[26] U.S. Pat. 1166576, 1916, *J.*, 1916, 255.
[27] Eng. Pat. 8673, 1915, *J.*, 1916, 49.
[28] Eng. Pat. 10446, 1915, *J.*, 1916, 541.

suitable number of briquettes to the furnace. Special appliances are used for the mixing.

Effect of High-Tension Discharge.

F. F. S. Bryson[29] notes that in a Wehnelt electrolytic interrupter, used to produce a high-tension discharge, the glass holder of the electrode becomes pitted at the point where the platinum wire is sealed into the glass, a crater being formed round the wire with all kinds of glass. When two wires are fused into the same piece of glass, two independent craters are formed, one around each wire.

Devitrification of Glass.

An interesting case of devitrification of crystal glass is described by H. Le Chatelier.[30] The glass-works at Baccarat having been seized by the Germans, the furnace—containing molten crystal glass—was kept at about 800° C. for three weeks, and the fire then left to die out. The cold pots containing "quinquet" glass (and no others) were found to have a felted mass of hexagonal scales at the bottom, and above this was transparent glass with isolated spherulites composed of lamellar crystals of tridymite. The mixture used for "quinquet" glass was 300 kilos. Fontainebleau sand, 76 sodium bicarbonate, 14 potassium carbonate containing 20 % water, 200 red lead, 4 potassium nitrate, 4 arsenious oxide, and 2500 kilos. of cullet. This is the first case on record of the crystallization of silica in the devitrification of glass. This production of tridymite confirms the view that tridymite is stable at 800° C. and at other temperatures above that at which quartz exists, and suggests that cristobalite is a metastable variety, produced only when the inversion of the quartz is incomplete.

Some Special Glasses.

A. Granger discusses[31] the general characters of special glasses containing respectively baryta, zinc oxide, magnesia, alumina, boric acid, phosphoric acid, antimony, and arsenic. As regards barium glasses, A. Silverman[32] gathers together a large number of facts and opinions, including several analyses and results of physical tests.

E. C. Sullivan and W. C. Taylor[33] have prepared a glass adapted to give airtight joints with metal wires, and having a linear expansion of more than 0·000012 and the requisite fluidity when heated to 640° C.

[29] *Engineering*, 1916, **101**, 517; *J.*, 1916, 691.
[30] *Comptes rend.*, 1916, **162**, 853; *J.*, 1916, 738.
[31] *Monit. Scient.*, 1915, **82**, 274; *J.*, 1916, 177.
[32] *J.*, 1915, 399.
[33] U.S. Pat. 1151911, 1915, *J.*, 1915, 1251.

It is composed of about 42 % silica, 19 % soda, 5 % potash, 19 % barium oxide, and 15 % alumina.

O. Schott,[34] of Jena, describes two boro-silicate glasses.

A semi-translucent glass, containing undecomposed sulphate, is made, according to H. A. Schnelbach,[35] by fusing together in a batch a colourless foundation mixture or glass with compounds containing aluminium, fluorine, and a sulphate.

Another semi-translucent glass, according to H. C. Stiefel,[36] is made from the materials for a crystal glass, with the addition of magnesium phosphate and certain substances (like magnesium carbonate, etc.) which cause a continuous evolution of gas during fusion.

Optical Glass.

Attention has already been called to the work of the Institute of Chemistry's Glass Research Committee, which included optical glasses in the scope of its investigations, and also to the researches now in progress at the National Physical Laboratory. The two patents of O. Schott, previously alluded to, are for optical glasses. Mention must also be made of the recently published Cantor Lectures on Optical Glass[37] by Dr. W. Rosenhain. In these lectures there is a tolerably full discussion of this important branch of the glass industry. Stress is laid on the fact that, contrary to the popular notion, colour in any ordinary degree is not seriously detrimental to glass for optical purposes, and the use of "decolorizers" (involving increased absorption of light) in most cases results in the production of inferior optical glass. On the contrary, quite apart from the presence of impurities, colour is inherent in good optical glass, and is closely associated with its most characteristic properties—besides transparency—of refraction and dispersion. Of great importance also in such glass is durability, which depends on resistance to the chemical action of air, moisture, or substances which may be deposited on the surface (such as organic dust, etc.). Other sources of difficulties (bubbles, devitrification, striæ, etc.) are considered at some length. The possibility of adopting the electric furnace for the commercial production of optical glass is suggested as a promising object of research. Another desideratum is to be able to make the glass pots of material (possibly of the carborundum class) insoluble in the molten glass, or, failing complete attain-

[34] U.S. Pats. 1130767 and 1143732, 1915, *J.*, 1915, 425, 834.
[35] U.S. Pat. 1143788, 1915, *J.*, 1915, 834.
[36] U.S. Pat. 1153353, 1915, *J.*, 1915, 1055.
[37] *Cantor Lectures on Optical Glass*, London, 1916.

ment of this ideal, to diminish the solubility as much as possible by protective coatings.

Ceramic Research.

The clay industries, like the glass industry, have been greatly affected by the exclusion from British markets (and those of our allies) of German and Austrian ceramic products. Much inconvenience resulted from the complete stoppage of the supply of laboratory porcelain ware, and the need for the provision of an efficient substitute soon became urgent. The difficulty has been met to a considerable extent by private enterprise, the efforts of several firms (including Doulton & Co., Ltd., Lambeth, and the Royal Worcester Porcelain Co., Ltd.) having been attended with promising results in this new field of activity. It is, of course, premature to speak definitely as to how the ware will compare with the German porcelain when it is used regularly in the laboratory. However, the National Physical Laboratory reported on some of these British products in very high terms. It may be added that, though not so widely known, similar ware has been produced by Macintyre & Co., Ltd., of Burslem, which appears to meet the ordinary tests quite as well as any other British ware of this type. Porcelain for laboratory ware has also been the subject of experiments by Bullers, Ltd., Hanley; Kirkham, Ltd., Stoke-on-Trent; Taylor, Tunnicliff & Co., Hanley; and S. T. Wilson, Stoke-on-Trent.[38] Dr. J. W. Mellor, Principal of the Stoke Pottery School, has also carried out independently important research work in this direction. It is gratifying to know that, on the recommendation of the Committee of the Privy Council on Scientific and Industrial Research,[39] a substantial grant has been made for the erection and maintenance of research laboratories and a small factory equipment in connection with the well-known Pottery School at Stoke-on-Trent. The construction of these is now in progress, and the research is to be carried out under the direction of Dr. J. W. Mellor, with the co-operation of Mr. Bernard Moore, a practical potter of wide knowledge and experience. One of the first subjects for investigation is to be the hard porcelain suitable for domestic ware, with the object of facilitating its production in this country on a manufacturing scale. It may be noted that Dr. Mellor has for some time past been successfully producing, in connection with the Pottery School, the Seger cones required by some manufacturers for indicating the progress of the heating during firing operations. This may be taken as an augury of complete success in the larger enterprise.

[38] *Proc. Inst. Chem.*, 1914, Part 4, 7. [39] *J.*, 1916, 913.

It is not generally known that hard porcelain was regularly made in England more than a century ago, but it was gradually ousted by the English bone china, first produced about the middle of the eighteenth century. Disregarding the fine stoneware (some of which showed a distinctly porcellanous nature) made by Dwight at Fulham in the seventeenth century, the manufacture of hard porcelain was commenced at Plymouth in 1768 by William Cookworthy, and afterwards continued by him at Bristol, where he was succeeded in 1775 by Richard Champion, who had purchased Cookworthy's patent. Some two or three years later Champion sold his patent to a company of Staffordshire potters, who carried on the manufacture at the New Hall Works, Hanley, until 1810 or 1812, when it was superseded by bone china. In more modern times the famous firm of Mintons, at Stoke-on-Trent, produced hard porcelain of good quality for a short time about 1849, in accordance with English Patent 8124, June 22, 1839, but excessive loss in firing (mainly owing to unsatisfactory saggers) caused its abandonment.

Ceramic Bodies and Raw Materials.

The mention of hard porcelain in the preceding paragraph recalls an article by R Rieke[40] on the properties of the porcelain made at the Royal Porcelain Factory, Berlin, dealing somewhat in detail with its composition and more important physical properties. It is remarkable that, while the specific gravity of the fully burned ware (fired up to 1420° C.) is 2·465, that of unglazed porcelain burned at 950° C. is 2·64, the specific gravity being thus diminished during the burning. Its resistance to sudden changes of temperature is due to the relatively low coefficient of expansion, which is less than that of either ordinary glass, stoneware, or magnesia, etc. Crucibles and short tubes, etc., if properly supported, can be used up to 1400° C., at which temperature pyrometer tubes of Berlin porcelain remain quite impermeable under ordinary atmospheric pressure.

J. W. Mellor's notes on hard or felspathic porcelain[41] present an illuminating general discussion, with special reference to the possibility of establishing the manufacture in our own country of a similar, but not necessarily identical, product, using as far as practicable British materials and the British traditional methods.

E. Rosenthal,[42] in discussing the technical properties of porcelain with

[40] *Z. angew. Chem.*, 1915, **28**, 374; *J.*, 1915, 1093.

[41] *Trans. Eng. Ceram. Soc.*, 1914-15, **14**, 176; *J.*, 1916, 539.

[42] *Tech. Studien*, No. 17 (35 pp.); *Z. angew. Chem.*, 1915, **28**, Ref. 598; *J.*, 1916, 178.

special reference to its use as insulator, states that the insulating power is not seriously affected by change in chemical composition, but is diminished when relatively large amounts of felspar are used, the reduction then being due to the presence of microscopic bubbles. He points out that economy could be effected, without sacrificing the valuable electrical and mechanical properties, by using less felspar and cheaper clay.

In an investigation of the viscosity of porcelain bodies high in felspar, A. V. Bleininger and C. S. Kinnison[43] concluded that a high proportion of clay reduces the elongation under tensile stress at high temperatures, and that the effect of flint is inappreciable.

L. J. Truss and P. Stanway[44] studied the relation between the composition of an earthenware body and crazing or peeling of the glaze. The results obtained under specified conditions are tabulated and summarized in a triangular diagram. Further investigation is contemplated.

I. J. B. Darget[45] claims that the addition of natural hydrated magnesium silicates to clay gives a light-coloured ceramic body, which works well, does not crack or contract, and yields pottery which is only slightly porous, and need only be glazed when the articles are to contain liquids.

O. Kallauner and J. Matějka[46] give detailed instructions for determining the rational analysis of clay from ordinary chemical analysis.

J. Dorfner[47] contends that the so-called rational analysis is unsatisfactory for the examination of fine clays or bodies, as it does not indicate the nature and amount of the "clay substance" nor the refractoriness of the material, and it is useless for coarser clays. It only gives approximately correct results with the purest kaolins, and its use in calculating the formulæ of other clays is not permissible. An accurate chemical investigation of clays and bodies in general can only be made by means of an ultimate analysis, the formula calculated from such an analysis of the finest particles of a completely homogeneous sample indicating satisfactorily the true composition of the fluxes, the ratio of basic to acid constituents, the probable behaviour of the material when heated, and the relative proportions of the refractory and fusible constituents. Some general conclusions are given relating

[43] *J. Franklin Inst.*, 1915, **180**, 232; *J.*, 1915, 906.

[44] *Trans. Eng. Ceram. Soc.*, 1914–15, **14**, 173; *J.*, 1916, 539.

[45] First addition, dated Apr. 4, 1914, to Fr. Pat. 456459, June 25, 1912, *J.*, 1915, 178.

[46] *Sprechsaal*, 1914, **47**, 423; *J.*, 1915, 963.

[47] *Ibid.*, 1915, **48**, 209; *Z. angew. Chem.*, 1916, **29**, Ref., 105; *J.*, 1916, 602.

to the effect of varying proportions of potash and lime in the composition of porcelain and stoneware bodies.

P. Rohland[48] states that the rapid deposition of quartz and sand particles from a suspension of raw kaolin on addition of a little solution of alkali silicate cannot be attributed to the influence of the colloidal silicic acid or the hydroxyl ions which are formed as a result of the hydrolysis of the silicate, but must be ascribed to the action of the undissociated alkali silicate in the colloidal state. This action causes an increase in the degree of dispersion of the kaolin particles, and the settling out of the quartz and sand particles is a consequence of this physical change.

Rohland[49] also asserts that the behaviour of kaolins towards organic dyes, viz., their adsorption capacity, may be employed in forming an estimate of the suitability of the kaolins for use in the ceramic and paper industries.

A. V. Bleininger[50] concludes that in Schwerin's electro-osmosis process for purification of clays, the essential feature is the preliminary treatment with caustic soda or other electrolyte; electro-osmosis plays no part in the purification of the clay, but merely regulates the density of the deposit on the positive electrode. Air, entrapped when clay slip is prepared, has a marked effect on the viscosity, and must be removed by stirring. The present writer once had to deal with an extreme case of ball clay slip (in an ordinary sliphouse blunger), which was so thoroughly impregnated with minute air-bubbles that the material could not be poured or run off as usual, and a pint of it actually weighed less than the same volume of water (20 oz.) instead of being 4 oz. more. In this instance ordinary agitation failed to remove the trouble, which, however, soon yielded to the influence of steam on introducing a branch pipe into the blunger. The viscosity of slips made of several clays is irregular. Ball clay is particularly objectionable in a slip to be used for casting.

In Schwerin's process[51] for separating fine particles from admixed coarser material, the clay or other substance is suspended in water (or other suitable medium), and an electrolyte, such as ammonia, is added, which causes the finer particles to pass into the sol state, whilst the coarser particles either separate in the gel state or form a sol of a lower degree of stability than that of the finer particles. The mixture is then subjected to centrifugal force to effect a fractional separation of the

[48] *Kolloid Zeits.*, 1914, **15**, 158; *J.*, 1915, 661.
[49] *Ibid.*, 1914, **15**, 180; *J.*, 1915, 654 and 661.
[50] *J. Franklin Inst.*, 1915, **180**, 225; *J.*, 1915, 906.
[51] Eng. Pat. 7590, 1915; *J.*, 1916, 729 and 738.

constituents. The separation of the components in the sol state may be facilitated by electro-osmotic action, the containing vessel forming one electrode, and the other being placed in the liquid.

As recorded by W. R. Ormandy,[52] certain North Staffordshire fireclays, after purification by this process on a fairly large scale, gave excellent results when made up into fireclay goods in the usual way, though it is within the writer's knowledge that exactly similar samples, without undergoing the special preliminary treatment, could not be relied on to furnish uniformly satisfactory products owing to the presence and irregular distribution of impurities. The writer personally carried out some experiments on a small scale, in which a S. Staffordshire fireclay, similarly purified, was completely substituted, weight for weight, for the ball clay in an earthenware body, and the resulting trial pieces after treatment in the usual way could scarcely be distinguished from the normal earthenware, except by a rather more pronounced yellowish tinge, which could easily be remedied by slightly increasing the amount of blue stain in the body mixture.

There is ample ground for the belief that this and other more or less similar processes offer great possibilities for certain clay industries when the nations are again in a position to devote close attention to peaceful pursuits.

J. L. Musser[53] suggests decanting the clay pulp from heavy impurities, heating it to expand the particles, and decanting off the light particles thus separated. The residual heated pulp is subjected to reduced pressure, and then dried.

W. J. Gee[54] claims the treatment of china clay or other material by passing an aqueous suspension of it through two centrifugal separators in succession. The first runs at relatively low speed, and separates the coarser particles, while the second completes the separation of the finer material.

W. Feldenheimer[55] proposes to feed an aqueous suspension of china clay (or the like) into a rotary cylindrical drum separator, which is mounted axially on a vertical spindle, and rotated at such a speed that the "mica," or heavier or coarser material, is retained in the separator, whilst the clay, or lighter or finer material, is discharged in suspension.

O. O. Erfurth[56] uses a purifier consisting of two cylindrical sieves arranged in line, within which work equally pitched right and left

[52] *Trans. Eng. Ceram. Soc.*, 1913-14, **13**, 42; *J.*, 1914, 257.
[53] U.S. Pat. 1147114, 1915; *J.*, 1915, 906.
[54] Eng. Pat. 24077, 1914, *J.*, 1916, 117.
[55] Eng. Pat. 24179, 1914, *J.*, 1916, 178.
[56] Eng. Pat 14358, 1915, *J.*, 1916, 310.

handed conveying worms, mounted on the same horizontal shaft. The clay, introduced at a central point, is carried by the conveying worms either one way or the other, and passes through one sieve, while stones, etc., collect in a receptacle at the end of the cylinder. By reversing the direction of rotation of the shaft, the clay is made to pass through the other sieve, so that the first can be cleaned without interrupting the process.

Richter and Richter[57] apply the method of preparing clay for the purification of effluents, etc., as described in their earlier patent, to the purification of clay and kaolin slips, for the purpose of removing sandy constituents and increasing the adsorptive power of the clay.

W. W. Simonson[58] proposes to refine kaolins and similar clays for use in making pottery and like products by treating the clay with an acid and a soluble copper salt, *e.g.*, sulphuric acid and cuprous chloride, with or without the addition of sulphurous acid, in order to reduce iron compounds and remove them from the clay.

F. Thompson[59] claims to remove iron from clays, etc., without decreasing plasticity, by treating with dilute hydrochloric acid under heat and steam pressure, the acid being either directly added or formed *in situ* by the action of another acid or an alkali chloride. It is interesting to note that a very similar method, but without heat and pressure, was proposed as long ago as 1859, by Joseph Bower, in Eng. Pat. 2691.

J. W. Mellor and B. J. Moore,[60] in an investigation of the effect of loads on refractoriness of fireclays, found that the reduction (with unit increase of load) of the softening or squatting temperature—which may result from diminution of the apparent viscosity, or from acceleration of the reaction between different minerals in the clay—is directly proportional to the squatting temperature. The relation is shown by the exponential equation: $T = Ce^{-kW}$, where T represents the squatting temperature (in degrees C. or in Seger cones), W the load (in pounds per square inch), C the squatting temperature without load, k a constant depending on the material (clay, etc.), and e is the regular exponential constant. The squatting temperature of china clay falls about one cone for every $5\frac{1}{4}$ lb. per square inch increase in the load. The more siliceous the clay the less is the difference between the squatting temperatures with and without load.

[57] Ger. Pat. 291834, 1913, *J.*, 1916, 842 (addition to Ger. Pat. 258152; see Fr. Pat. 443789, 1912, *J.*, 1912, 1025).

[58] U.S. Pat. 1185254, 1916, *J.*, 1916, 738.

[59] U.S. Pat. 1132537, 1915, *J.*, 1915, 426.

[60] *Trans. Eng. Ceram. Soc.*, 1915–16, **15**, 117; *J.*, 1916, 841.

J. W. Mellor and B. Moore[61] have studied the effects of heat, etc., on flint and quartz. Both materials as the result of calcination have their specific gravities considerably reduced, the reduction being finally greater for flint than for quartz, and the rate of change being much slower in the case of quartz, at all events in an English china biscuit oven at cone 10. The accompanying increase of volume has a much greater shattering effect in the case of flint than with quartz. The possibility of substituting flint by quartz, sand, etc., is discussed, and also the use of siliceous china and ball clays, etc., which might obviate the need for using flint in earthenware body mixtures.

J. West,[62] in discussing silica and fireclay materials, calls attention to a high-grade silica from Derbyshire, which, when made into bricks, was found to expand in length less than 1 % on heating to 1430° C.

W. Feldenheimer and W. J. Gee[63] propose to nullify discoloration due to impurity by converting part of the impurity into a colouring agent capable of neutralizing the remaining discoloration. In the case of china clay, the colouring effect due to iron or iron compounds is nullified by treating the clay with a very dilute solution (less than 1 %) of potassium or sodium ferrocyanide or other suitable cyanogen compound, whereby some of the iron is converted into Prussian blue.

To prevent blisters rising during drying of stoneware pipes, traps, etc., J. Brewin[64] proposes to mix some dry clay dust with the prepared pugged clay before using it.

Grinding of Ceramic Materials.

The fineness of grinding of pottery materials has an important bearing on the results obtained, and reference may be made to an instructive discussion which took place at a meeting of the English Ceramic Society.[65] In a recent patent,[66] F. T. H. Goodwin provides a baffle to arrest the motion of the water which carries along the ground material, and so promotes deposition of incompletely ground particles.

Ceramic Ovens and Kilns.

C. Dressler,[67] whose original tunnel oven was successfully used for firing glazed tiles, etc., has introduced modifications, which are not only

[61] *Trans. Eng. Ceram. Soc.*, 1915–16, **15**, 77; *J.*, 1916, 840.
[62] *J. Gas Lighting*, 1916, **134**, 442; *J.*, 1916, 691.
[63] Eng. Pat. 894, 1915, *J.*, 1916, 310.
[64] Eng. Pat. 10643, 1915, *J.*, 1916, 541.
[65] *Trans. Eng. Ceram. Soc.*, 1913–14, **13**, 114; *J.*, 1915, 139.
[66] Eng. Pat. 12202, 1915, *J.*, 1916, 255.
[67] *Trans. Eng. Ceram. Soc.*, 1914–15, **14**, 41; *J.*, 1916, 539.

improvements on the first form, but which make it available for much higher temperatures, so that it can be adapted even for biscuit firing.

A. Bigot,[68] in discussing the distribution of heat in ceramic ovens, compares the amounts utilized and wasted in three different types of oven, viz., Dressler tunnel oven, Hoffmann continuous oven, and ordinary intermittent oven. He concludes that the Dressler oven is much more economical than the others.

G. W. Ogan's kiln[69] for burning clay products is a semi-continuous kiln in which the heating gases enter and leave each chamber through openings in the floor, the chambers being connected by flues beneath the floor. The oven of Gibbons Bros., Ltd., R. Masters, and R. Baker,[70] is of the tunnel type, with passages for the producer gas and for air. The waste gases escape through passages in the floor to an underground flue leading to the chimney.

In the ceramic kiln of W. A. Norman and E. Evans,[71] there is a lower floor below the floor supporting the material, and the draught openings in the former are surrounded by short vertical pipes provided with detachable hoods to prevent obstruction by broken material. Plugs may be provided for stopping the pipes when a modification of the draught is desired.

Ceramic Glazes.

R. Rieke and W. Steger[72] found that the coefficient of expansion of a glaze, between the ordinary temperature and 100° C., was diminished by increasing the content of silica, by substituting silica for an equivalent quantity of boric acid, and by alumina up to a content of 0·3 molecule. It was increased by increasing the content of boric acid, and, in the case of borate glasses free from silica, by proportions of alumina exceeding 0·2 molecule. The coefficient of expansion of borate glasses containing very little or no silica was diminished by increasing the content of boric acid. There was no direct relation between the coefficients of expansion of the glazes and their behaviour when applied to pottery bodies.

R. Rieke and W. Steger[73] found in the case of porcelain glazes that the coefficient of expansion is greatest in the tender porcelains with a

[68] *Trans. Eng. Ceram. Soc.*, 1914–15, **14**, 96; *J.*, 1916, 540.

[69] U.S. Pat. 1147117, 1915, *J.*, 1915, 906.

[70] Eng. Pat. 16970, 1914, *J.*, 1915, 907 and 909.

[71] Eng. Pat. 5341, 1915, *J.*, 1916, 541.

[72] *Sprechsaal*, 1914, **47**, 577, 585, 593, 601; *Z. angew. Chem.*, 1915, **28**, Ref., 22; *J.*, 1915, 493.

[73] *Sprechsaal*, 1915, **48**, 381, 390; *Z. angew. Chem.*, 1916, **29**, Ref., 70; *J.*, 1916, 423.

low content of silica, and least in hard porcelains which are rich in alumina and silica. It increases proportionately with the fluxes, but independently of the alumina–silica ratio. Glazes with more than 9–10 mols. silica are turbid. Glazes with only 6–8 mols. silica or 0·3–0·4 mol. alumina tend to craze.

H. Harkort[74] discusses the relation of frit to glaze in stoneware glazes and its connection with glaze defects. He finds that defects like cloudiness, matt patches, etc., are generally caused by too high a proportion of lime in glazes on the better classes of goods, fired at a glost temperature of Seger cone 01 to 6. The lime should not exceed 0·4 eqvt. for 2·5 eqvts. silica. Dullness often arises from volatilization of boric anhydride from the glaze, especially under influence of sulphuric acid from furnace gases. The presence of calcium carbonate is a protection against sulphuric acid, and so reduces the risk of volatilization of boric acid. Lead oxide promotes the absorption of lime better when in the glaze than when in the frit only, but exerts no influence on the volatilization of boric acid. The author concludes that the content of lead oxide may be reduced and replaced by the cheaper calcium oxide, and that the lead oxide introduced into the glaze should be fritted. The use of non-sulphurous coal and regulating the conditions of firing can remedy certain of the defects.

C. Kabus[75] states that in the production of crystalline glazes with zinc silicate the cooling period should be long (as in ordinary industrial ovens) to give fine crystals, but with rutile the period should be short (as in muffle furnaces). An oxidizing atmosphere in the oven is much the best for crystalline glazes. Crystallization is much facilitated by the addition of ammonium vanadate, and of molybdic and tungstic anhydrides. Oxides of manganese, chromium, iron, etc., can be used for crystalline glazes. The proportions of these should be about half that of the total bases in Seger's formula.

Ceramic Colours.

Cobalt and nickel colours were studied by A. D. Hollinshead, J. Turner, and J. W. Mellor[76] by calcining a series of mixtures of cobalt and nickel oxides respectively with alumina, with zinc oxide, and with both of these together. The colours were printed on earthenware, and, after dipping in certain selected glazes, were fired in a glost oven. The equilibrium tint of cobalt blues under lead glazes and

[74] *Z. angew. Chem.*, 1915, **28**, 422; *J.*, 1916, 49.

[75] *Keram. Rundschau*, 1915, **23**, 139, 165, 178, 183; *Z. angew. Chem.*, 1915, **28**, Ref., 598; *J.*, 1916, 178.

[76] *Trans. Eng. Ceram. Soc.*, 1914–15, **14**, 167; *J.*, 1916, 540.

leadless glazes is the violet-blue of cobalt silicate, and other blue tints can be insured only within certain limited conditions (lower firing temperature, shorter period of firing, colour more or less protected from attack of silica or glaze, little or no solvent action of glaze on body). The nickel colours are too unstable when no other colouring material is present.

Brown colours prepared from mixtures of ferric and chromic oxides (equal parts) with varying proportions of china clay and zinc oxide were studied by J. R. Adderley,[77] who found that raw lead glazes gave the worst results, producing irregular variations. Fritted lead glaze gave the best results (practically uniform tints), while leadless glaze was intermediate. Increased china clay in the colour mixture gave much darker tints.

Chrome tin pink, according to J. W. Mellor,[78] has the same tint whatever compound of chromium be used in making it, providing it be fully developed in firing. The discrepancies in results obtained by other workers are due to incomplete development of the colour through under-firing. In Germany K. Jacob, quoted by J. W. Mellor,[79] had shown that boric oxide (in the glaze) does not act on underglaze pink if the proportion of lime be kept high. With 0·4 equivalent of lime, the boric oxide should not exceed 0·1 equivalent, and it should not exceed the proportion of alumina.

With reference to the reproduction of Egyptian blue, L. Bock[80] claims priority for the French ultramarine works of Deschamps Frères. It was obtained by fusing together 50 parts quartz, 21 parts chalk, 24·4 parts copper oxide, and 4·6 parts sodium carbonate, all very finely powdered and free from iron. The washed product was represented by the formula $CaO,CuO,4SiO_2$, and corresponded completely in chemical and physical properties with the ancient material. Laurie, McLintock and Miles[81] obtained a product similar in composition and properties by a similar process.

Enamels.

J. Weber[82] uses anhydrous calcium stannate as an opaque material for enamels and the like.

[77] *Trans. Eng. Ceram. Soc.*, 1915–16, **15**, 133; *J.*, 1916, 841.
[78] *Ibid.*, 1915–16, **15**, 131; *J.*, 1916, 841.
[79] *Pottery Gazette*, 1916, 174. See also *Sprechsaal*, 1915, **48**, 98, 107.
[80] *Z. angew. Chem.*, 1916, **29**, i, 228; *J. Chem. Soc.*, 1916, ii, 434.
[81] *Proc. Roy. Soc.*, 1914, A, **89**, 418; *J.*, 1914, 91.
[82] U.S. Pat. 1181944, 1916, *J.*, 1916, 691.

Very pure antimonates of white colour and voluminous structure are prepared, according to P. Eyer,[83] by heating oxides of antimony with one or more bases to a high temperature in the presence of ammonium nitrate. Antimonates thus made are specially valuable for clouding glasses and enamels, especially the antimonates of magnesium and zinc.

As an opacifying agent in place of the expensive tin oxide, good results have been obtained with preparations of zirconia, more particularly the silicate, in glazes with and without lead, and also in the enamel industry. An extensive deposit of earthy zirconia in Brazil was entirely under German control, and was worked according to a German patent to produce a preparation known commercially as "terrar," which was either included in the frit or added to the mill mixture in the case of glazes.[84] The raw material is now available to British consumers, and it may be well to add that a licence to work the patent has been granted to a Stoke-on-Trent dealer.

De Haën has made use of Baezner's patent[85] for an opaque enamel or glaze, the vitrifiable material being mixed with zinc sulphide. This can only be used at comparatively low temperatures, and, of course, lead cannot be present if dark coloration is to be avoided.

[83] Eng. Pat. 11083, 1915, *J.*, 1916, 839 and 842.

[84] *Sprechsaal*, 1916, **49**, 112.

[85] U.S. Pat. 1153748, 1915, *J.*, 1915, 1055.

BUILDING MATERIALS.

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Refractory Materials.

A series of researches on refractory materials projected by the Institution of Gas Engineers is now in progress at the Stoke-on-Trent Central School of Science and Technology under the direction and superintendence of Dr. J. W. Mellor. A brief notice of a preliminary investigation will be found in the "Glass and Ceramics" section, p. 139. It is also interesting to note that zirconia is under investigation at the National Physical Laboratory, and also at Sheffield University. Its use as a refractory has been under consideration for some time past, particularly in Germany.[1]

In the production of high grade refractories and heat-insulating materials attempts have been made to utilize carborundum and similar substances composed mainly of silicon and carbon, and some of the so-called rarer earths (other than zirconia) have also been brought into requisition.

E. W. Weintraub[2] describes a new heat insulator termed fibrox, a silicon oxycarbide, prepared by melting silicon with a catalytic agent, such as calcium fluoride, in a muffle or crucible, carbon monoxide and dioxide diffusing slowly through the containing vessel and combining with the silicon to form a soft, resilient, fibrous material. The specific gravity of the fibres is 1·8 to 2·2, and the apparent density is 0·0025 to 0·0030, more than 99 % of the space being occupied by air. The heat-insulating capacity is said to be equal to that of compressed wool of fifteen times greater density.

Maywald[3] prepares a fine-grained, cellular, heat-insulating material by gradually introducing a soluble silicate in liquid form, by means of

[1] *E.g.*, see article by O. Ruff, H. Seiferheld, and O. Bruschke, *Z. anorg. Chem.*, 1914, **86**, 389; *J.*, 1913, 866, and 1914, 593.

[2] *Amer. Electrochem. Soc.*, April, 1915; *Met. and Chem. Eng.*, 1915, **13**, 315; *J.*, 1915, 615. See also U.S. Pat. 1094352, 1914, *J.*, 1914, 594.

[3] U.S. Pat. 1142829, 1915, *J.*, 1915, 836.

an atomizer, into a mould rotating very rapidly. The mould is heated in order to bake, expand, and harden the material.

Scharwath[4] prepares a heat-insulating material by alternately coating a core with solution of alkali silicate, and heating the coating to harden it, until a sufficient thickness is obtained.

S. A. Tucker and A. Lowy[5] describe an electric furnace product known as silundum,[6] obtained by the action of silicon vapour or a mixture of silicon vapour and carbon monoxide on carbon at temperatures above 1300° C. Up to about 1800° C. a greenish slate-coloured variety of silundum is formed, having the composition Si_4C_4O. Above 1800° C. the product is steel-grey, having the composition SiC, and is apparently a form of carborundum. Above 2200° C. silundum is decomposed, graphite being formed. Silundum has specific gravity 2·9–3, hardness about 9, and it is a good conductor of electricity.

Lecesne[7] proposes to prepare refractory materials by first heating bauxite with anthracite under gradually increasing pressure until the bauxite is melted. For impervious refractory articles the product (which is very porous and of low density) is mixed with water, ground quartz, and a little quicklime, the two latter combining to form a bond. For porous refractory goods raw bauxite is used as a bond.

A highly-refractory material has been prepared from a mixture of about equal parts of zirconia and carborundum,[8] in which the latter is coarser-grained than the former. The mixture is moulded into shapes, which are then burnt. Such a mixture is said to show none of the tendency of zirconia to crack and lose mechanical coherence.

A refractory mixture for zinc muffles[9] is made of 1 %–10 % zirconia, 33·3 % clay, and burnt fireclay (grog).

Another suggestion[10] is to coat a fireclay brick with refractory material of high thermal conductivity (as carborundum), the same material being also used to fill openings passing through the brick from side to side.

A somewhat similar notion is applied by Sidebottom[11] in lining crucibles with yellow sand, previously mixed with about 7 % of gas tar and baked for five hours at 93° C.

[4] U.S. Pat. 1178027, 1916, *J.*, 1916, 635.

[5] *J. Ind. Eng. Chem.*, 1915, **7**, 565; *J.*, 1915, 835.

[6] See Bölling, *J.*, 1909, 27.

[7] Fr. Pat. 471513, 1914, *J.*, 1915, 356.

[8] U.S. Pat. 1159264, 1915, *J.*, 1915, 1252. See also Eng. Pat. 4080, 1915, *J.*, 1916, 842.

[9] Ger. Pat. 287122, 1913, *J.*, 1916, 178 and 185.

[10] Ger. Pat. 286206, 1914, *J.*, 1916, 180.

[11] Eng. Pat. 2578, 1915, *J.*, 1916, 361.

It may here be noted that many years ago Engels[12] applied a mixture of silica and carbon to the surfaces of bricks, and to walls of furnaces, etc., and fused it by an electric arc to form a fire-proof and acid-proof covering of carborundum or silicon carbide.

As a binding material for carborundum, Vail and Carter[13] propose to use an alkaline solution of a silicate in which an oxidizing agent (such as potassium permanganate) is dissolved; the mass is then baked in moulds at a relatively low temperature. For the same purpose Allen[14] proposes magnesium aluminium silicate or magnesium aluminium borosilicate, the mixture being raised to the vitrifying point.

For the manufacture of porous refractory masses for flameless surface combustion Knöfler[15] recommends the use of zirconium oxide, with or without titanium oxide.

Parts of highly refractory ceramic objects to be coated with refractory rare earths (zirconia, thoria) are, according to Herzfeld's process,[16] first covered with a thin layer of a mixture of the body material and the rare earth, and then with the rare earth itself, and the whole fired. The layers of rare earths may be deposited by electro-osmosis.

Silica Bricks.

Silica bricks, especially those intended for the by-product coke-oven, are discussed by K. Seaver.[17] With less than 2 % of lime (added as milk of lime during grinding of the crushed material) the strength of the finished brick is reduced, and with more than 2 %, refractoriness and resistence to abrasion are reduced. When no flux or catalyst is present, quartz is converted directly into cristobalite at 1000° C., the change taking place very rapidly at 1300° C., without intermediate formation of tridymite; this change is associated with 13·4 % increase of volume. In practice the permanent expansion produced by burning is $\frac{3}{8}$ inch per foot. Seaver concludes that in burning as practised at present the quartz-cristobalite inversion is effected to the greatest degree economically possible. With repeated burnings, the percentages of cristobalite in the case of silica brick were found to be 77, 83, and 84 respectively after the first, second, and third burning, whilst in the case of quartz rock the corresponding percentages were 49 and 69 after

[12] Eng. Pat. 24378, 1898.

[13] U.S. Pat. 1139739, 1915, *J.*, 1915, 717.

[14] U.S. Pat. 1172659, 1916, *J.*, 1916, 470.

[15] Ger. Pat. 284395, 1914, *J.*, 1915, 1081 and 1093.

[16] Ger. Pat. 289992, 1914, *J.*, 1916, 541.

[17] *Amer. Inst. Min. Eng.*, Sept. 1915; *Met. and Chem. Eng.*, 1915, **13**, 861; *J.*, 1915, 1209.

first and second burning. In the re-burned silica brick the grains consisted essentially of cristobalite with quartz as an inclusion. The strength of the brick was increased by re-burning.

In considering the raw materials for silica bricks, A. K. Khoétsky[18] states that the value of natural silica for making bricks depends on chemical purity, size of grain, and low expansion on heating. To withstand a temperature of 1700° C., the brick must contain at least 96 % silica, and the raw material must therefore contain 98 % silica. The raw material should not give too fine a powder on crushing, for bricks composed of fine grains are not porous enough, and break down on being heated. Schistose quartz (on account of its structure and the presence of many impurities as inclusions), and sandstones and sand (because of variable composition and too great fineness after being ground), are declared to be unsuitable for the manufacture of silica bricks.

Raw kieselguhr has been proposed by Hesselmeyer[19] as the sole ingredient of bricks.

Refractory Furnace Linings, etc.

Refractory material suitable for furnace linings, etc., is produced by Hershman[20] by mixing a substance (such as alumina), capable of forming a refractory carbide, with a hot carbonaceous binder (such as melted tar), and heating in an inert atmosphere slowly and gradually to at least 1500° C., but preferably to 2000° C.

Torsen[21] mixes 40 to 50 parts of a refractory compound of silica and carbon with 15 to 25 parts of fireclay, and 33 to 48 parts of silica. Meyer[22] mixes granulated hard burnt dolomitic lime with sufficient granulated basic open hearth slag as a binder to fill the voids between the granules of lime. Newberry[23] mixes coarsely pulverized cement clinker with water and 10–20 % calcium chloride, the mixture being shaped into blocks and dried.

Hillis[24] advocates the use of a furnace brick made of about 20 % ground flint, 10 % plastic clay, 30 % carborundum, and 40 % binding clay.

[18] *Rev. Soc. russe de Métall.*, 1914, **1**, 170; *Rev. Mét.*, 1915, **12**, 143; *J.*, 1915, 1055.

[19] U.S. Pat. 1143826, 1915, *J.*, 1915, 835.

[20] Eng. Pat. 17447, 1915, *J.*, 1916, 692; also U.S. Pat. 11351182, 1915, *J.*, 1915, 836.

[21] U.S. Pat. 1167135, 1916, *J.*, 1916, 256.

[22] U.S. Pat. 1160085, 1915, *J.*, 1915, 1252.

[23] U.S. Pat. 1156018, 1915, *J.*, 1915, 1132 and 1146.

[24] U.S. Pat. 1168211, 1916, *J.*, 1916, 311.

A special refractory brick for lining rotary cement kilns[25] for resisting unduly rapid corrosion by the clinker when a layer of non-conducting material is placed between the outer casing and the refractory lining (to reduce loss of heat by radiation), contains over 60 % of fused alumina.

The use of nitrides of boron, titanium, etc., is recommended by Podszus[26] for the construction of furnaces, and for crucibles to melt metals in. They are declared to be capable of withstanding very high temperatures, and also changes of temperature, and of retaining their electrical insulating capacity, even at the highest temperatures.

Grog.

For the production of "grog," Bertram[27] proposes to make clay into a slip with water, mix with it a large proportion of combustible material, then dry and burn it. Even when strongly heated, the product is very friable.

Purification of Refractory Materials.

In the report on "Glass and Ceramics" reference is made to certain recently introduced processes for purification of clays, including fireclays. The latter can thus be greatly improved at a moderate additional cost, and it is possible that some of these processes may be found adaptable to certain other refractory materials.

Thermal Conductivity of Refractory Materials.

The importance of thermal conductivity at high temperatures being recognized, special attention has been bestowed on the conductivity of certain refractory substances by several investigators.

Heyn[28] describes the method of testing followed in the *Kgl. Materialprüfungsamt* at Berlin. Dudley[29] gives results of determinations made for fireclay, silica (clay bond and lime bond), and magnesite. G. H. Brown[30] has determined the relative thermal conductivities of silica and clay refractories, and found that fireclay bricks had less conductivity than bricks made of silica (quartzite, etc.), and that of

[25] Fr. Pat. 472033, 1914, *J.*, 1915, 426.

[26] Ger. Pats. 282748 and 286992, 1913, *J.*, 1915, 717; 1916, 176 and 178.

[27] Ger. Pat. 288721, 1914, *J.*, 1916, 424.

[28] *Stahl und Eisen*, 1914, **34**, 832; *Z. angew. Chem.*, 1914, **27**, Ref., 722; *J.*, 1915, 426.

[29] *Amer. Electrochem. Soc.*, April, 1915; *Met. and Chem. Eng.*, 1915, **13**, 315; *J.*, 1915, 615.

[30] *Trans. Amer. Ceram. Soc.*, 1914, **16**, 382; *J.*, 1914, 1052.

two of the latter bricks (containing respectively 95 % and 83 % silica) the one with most silica showed a higher degree of conductivity.

Dougill, Hodsman, and Cobb[31] have carried out a more elaborate research and discussed the question more fully; they used specially devised apparatus and tested ordinary bricks and blocks, etc., instead of smaller pieces. They found that hard fired bricks (at cone 10–11) had much greater conductivity than similar fireclay bricks fired at a lower temperature (cone 8–9), and that silica bricks had greater conductivity than siliceous bricks with a smaller percentage of silica. The hard fired clay bricks had conductivity practically equal to that of the silica bricks. Magnesite bricks showed much greater conductivity than the other kinds. The conductivity of joints was much less than that of bricks.

Refractory Bricks.

Some of these have already been alluded to incidentally. Ingvaldsen[32] produces a refractory electrically-insulating brick from a mixture of finely divided mica and quartz, with just enough clay, or similar binding material, to form a plastic mass, the mixture being moulded and afterwards burnt so as to fuse the mica. The resulting refractory brick is specially suited for use in electric furnaces.

Crawford[33] proposes to heat a mixture of about 82 % finely divided silica and 18 % refuse oil from mineral oil stills to 2000° C. in a reducing atmosphere. The carbonaceous clinker so obtained is powdered and mixed with a concentrated solution of sodium silicate, the product being moulded and dried. To produce bricks, etc., for the highest temperatures, about 15 % of finely divided tungstic oxide is included in the mixture.

Léger[34] produces refractory bricks from a mixture of granulated and powdered silica and calcined magnesia, with a solution of magnesium chloride.

According to Grundmann[35] the binding power of magnesia is increased by treatment with steam. Reference may also be made here to the German sintered magnesite.[36]

[31] *J.*, 1915, 465. [32] Ger. Pat. 285482, 1913, *J.*, 1915, 1146.
[33] Eng. Pat. 18439, 1914, *J.*, 1915, 964.
[34] Fr. Pat. 472640, 1914, *J.*, 1915, 494.
[35] Ger. Pat. 290799, 1912, *J.*, 1916, 603. See also Ger. Pat. 291686, 1913, *J.*, 1916, 843.
[36] Ger. Pat. 291913, 1915, *J.*, 1916, 843. See also Ger. Pat. 288262, *J.*, 1916, 180.

Special Bricks.

Léger[37] makes bricks by pressing a mixture of eight parts of sand (not argillaceous), one part of barium sulphate, and one part of calcined magnesia, with enough magnesium chloride solution to form a bond. The bricks may be used after drying for twenty-four hours in the open air, and are quite dry after exposure for a week; they are impervious and not affected by water.

Dard[38] makes bricks similar to sand-lime bricks, with argillaceous sand or with clay.

Marz[39] produces bricks of uniform deep red colour by pressing close together in pairs the moist bricks from the press, with a sheet of air-tight paper between the faces of the bricks; the double bricks are dried and burnt, and then separated. The red colour thus obtained extends to a sufficient depth for practical purposes.

Disintegrating Effect of Brine.

An interesting record of the softening effect produced on mortar and brickwork by the prolonged infiltration of brine is furnished by Camilla,[40] the result being the collapse of a vault in a large warehouse at Turin.

Brick Kilns.

Brief reference may be made to two American patent brick-kilns,[41] of which one is a gas-fired kiln with the air preheated, and the other has a (circular) wall consisting of a metallic shell with a thin lining of refractory material.

Cement and Lime Kilns.

In a gas-fired rotary kiln for burning cement, lime, etc., Johanssen[42] arranges the burner at the end of the kiln so that it may be moved in various directions at will.

A kiln of Swiss origin[43] for burning cement, lime, etc., is a shaft kiln with an automatic rotary grate arranged as a boring device, or with a fixed grate and rotary borer and ribs above it. The borer perforates the clinker, separates the pieces, and delivers them to the ribs, which discharge them uniformly from the kiln.

[37] Fr. Pat. 472532, 1914, *J.*, 1915, 493.
[38] Fr. Pat. 475328, 1914, *J.*, 1916, 49.
[39] Ger. Pat. 292187, 1914; *J.*, 1916, 843.
[40] *Annali Chim. Appl.*, 1915, **4**, 145; *J.*, 1915, 1209.
[41] U.S. Pats. 159062 and 159539, 1915, *J.*, 1915, 1252.
[42] U.S. Pat. 1177865, 1916, *J.*, 1916, 635.
[43] Eng. Pat. 10388, 1915, *J.*, 1916, 891.

Constitution of Cement Clinker.

The constitution of Portland cement clinker has frequently been the subject of investigations, the results of which have led to diverse conclusions, largely owing to the effects of variations in the conditions. E. D. Campbell[44] found that celite is a calcium aluminate, which, when melted (at a little above 1400° C.), dissolves calcium oxide and calcium orthosilicate. The residue of the clinker (alite) consists mainly of α- or β-calcium orthosilicate, with calcium oxide and a certain amount of calcium aluminate and ferrite in solid solution. This view was supported by the synthetic production of celite[45] along with large crystals of alite, the latter being mainly $3CaO, SiO_2$; the celite was mainly $5CaO, 3Al_2O_3$. The general formula $x(3CaO, SiO_2) + y\ (5CaO, 3Al_2O_3)$ is suggested for Portland cement, and it is claimed that this formula conforms more closely with the results obtained in practice than those of Le Chatelier and Newberry.[46] Campbell concluded[47] that ferric oxide is molecularly equivalent to alumina in regard to the formation of celite, but whereas alumina acts only as an acid oxide, the ferric oxide apparently tends to replace part of the lime in the tricalcium silicate (alite).

E. Jänecke[48] adduces thermal and microscopical evidence for his view that the chief constituent (alite) of Portland cement has the composition $8CaO, Al_2O_3, 2SiO_2$. He explains the difference between this and the composition of normal clinker by stating that the latter is not in equilibrium because of an insufficiently high temperature of calcination. H. Kuhl[49] had previously come to the conclusion, from results of his own investigation, that alite is not Jänecke's compound, but a solid solution of which this compound forms the basis.

G. A. Rankin and F. E. Wright,[50] from the results of an elaborate investigation of the ternary system $CaO—Al_2O_3—SiO_2$, concludes that Portland cement clinker is essentially a mixture of $3CaO, SiO_2$; $2CaO, SiO_2$; $3CaO, Al_2O_3$, with some $5CaO, 3Al_2O_3$, and possibly free CaO. This conclusion obtains confirmation from the results of work carried out by P. H. Bates.[51] In a recently published article, G. A. Rankin[52] deduces from the foregoing results that the formation of the constituents

[44] *Tonind. Zeit.*, 1913, **37**, 1907; *J.*, 1914, 25.
[45] *J. Ind. Eng. Chem.*, 1914, **6**, 706; *J.*, 1914, 964.
[46] *J.*, 1897, 887.
[47] *J. Ind. Eng. Chem.*, 1915, **7**, 835; *J.*, 1915, 1093.
[48] *Z. anorg. Chem.*, 1914, **39**, 355; *J.*, 1915, 81. See also *J.*, 1912, 491.
[49] *Tonind. Zeit.*, 1914, **38**, 365; *J.*, 1914, 315.
[50] *Amer. J. Sci.*, 1915, **39**, 1; *J.*, 1915, 139.
[51] *Trans. Amer. Ceram. Soc.*, 1913, **15**, 420; *J.*, 1914, 81.
[52] *J. Franklin Inst.*, 1916, **181**, 747; *J.*, 1916, 842.

of Portland cement takes place as follows:—The free lime formed from the calcium carbonate unites with the clay, forming $5CaO, 3Al_2O_3$ and $2CaO, SiO_2$; these afterwards unite with more lime and form $3CaO, Al_2O_3$, and $3CaO, SiO_2$, the reaction being facilitated by the formation of a flux at 1335° C.—the eutectic temperature of $2CaO, SiO_2$; $5CaO, 3Al_2O_3$; and $3CaO, Al_2O_3$. As the temperature rises above 1335° C., any free lime present reacts with the $2CaO, SiO_2$, forming $3CaO, SiO_2$. It is not necessary to proceed to complete fusion, a temperature of 1650° C. being usually sufficient for commercial materials. At this temperature the mixture consists of 30 % molten and 70 % solid material, but on cooling the clinker is completely crystalline, and contains about 45 % of $3CaO, SiO_2$, 35 % of $2CaO, SiO_2$, and 20 % of $3CaO, Al_2O_3$. The percentage of $3CaO, SiO_2$ is the chief factor in determining the value of a Portland cement. It is the last substance to be formed, and under ordinary conditions the maximum obtained is 35 %. The proportion depends on the temperature, duration of heating, amount of fluxing oxides present, and the size of the particles. The use of more free lime (from limestone) would produce more $3CaO, SiO_2$, with higher temperature and longer heating, but the finished cement might then contain free lime. Instead of a higher burning temperature (which is impracticable commercially), a material richer in fluxes would induce the reaction $CaO + 2CaO, SiO_2 = 3CaO, SiO_2$, below 1650° C., the temperature required with the usual materials being much higher.

In a petrographic study of Portland cement, R. J. Colony[53] observed in fresh cement, besides fragments of residual clinker, isotropic hydrated grains, and crystalline (spherulitic) calcium hydroxide, another component (designated the "primary colloid") occurring in small areas, intimately mixed with the calcium hydroxide, and possessing a lamelloid structure. Within 5 or 6 days after gauging the cement, a secondary action occurred, resulting in the formation of a dense structureless mass called the "amorphous constituent," which obscured everything except the fragments of residual clinker, and apparently resulted from the interaction of the other three primary hydration products. Free calcium hydroxide was only visible as a lining of vesicles and cavities. After storing cement under water for a long time, the amorphous constituent was found to undergo partial crystallization, the products being secondary crystalline calcium hydroxide, calcite, and zeolitic matter.

From a petrographic study of the changes taking place in the

[53] *School Mines Quarterly*, 1914, **36**, 1; *J.*, 1915, 801.

aluminates and silicates which are constituents of Portland cement, when hydrated in different ways on microscopic slides, A. A. Klein and A. J. Phillips[54] conclude that the process of hydration in cement is as follows: amorphous hydrated $3CaO, Al_2O_3$ is formed, with or without amorphous alumina, and crystallizes later. At the same time sulpho-aluminate crystals are formed, and lime (low-burned or finely ground) is hydrated. These reactions begin within a few hours after the cement is gauged. The next compound to react is $3CaO, SiO_2$, the hydration of which may begin within 24 hours, and is generally complete within seven days. Between a week and a month the amorphous aluminate commences to crystallize, and hydration of $\beta 2CaO, SiO_2$ begins. This last-named compound is regarded as the chief constituent of American Portland cement, and it is the slowest to react. The early strength of cements (after 24 hours) is ascribed to hydration of lime and aluminates. Increase in strength between one and seven days depends upon hydration of $3CaO, SiO_2$, though further hydration of aluminates may also contribute. Increase between 7 and 28 days is due to hydration of $\beta 2CaO, SiO_2$, but is counteracted by hydration of high-burned free lime and crystallization of aluminates, which may cause a decrease in strength during this period. Finally iron compounds in cement resist hydration and occur as a rust-like material. The disintegrating action attributed to crystallization of the sulpho-aluminate $3CaO, Al_2O_3, 3CaSO_4, xH_2O$, is said to have been greatly exaggerated, as such crystals are extremely small, and they begin to form before the cement mass has assumed any great rigidity.

Fineness of Portland Cement.

An apparatus devised by officers of the U.S. Bureau of Standards[55] for determining the fineness of cement and other hard-grained materials, consists of a long vertical brass pipe with a glass bulb attached to the lower end. The cement or other material to be tested is placed in the bulb, and air at constant pressure is blown into it through a glass tube or nozzle in the side of the bulb. The moving air carries the cement dust to the top of the pipe, where it is caught in a flannel hood, and all the dust is removed in a short time.

Different grades of the fine material are obtained by using different sized nozzles. The size of the largest particles in any given separation can be readily determined with the aid of the microscope, and so the apparatus can be standardized without regard to size of nozzles and other parts of the apparatus, or the air pressure used.

[54] *Trans. Amer. Ceram. Soc.*, 1914, **16**, 313; *J.*, 1914, 1052.
[55] *U.S. Comm. Rep. No.* 208, Sept. 4, 1915; *J.*, 1915, 1011.

Hydraulic Modulus and Clay Index of Cement.

F. Ferrari[56] advances the view that the hydraulic modulus, *i.e.*, the ratio $CaO : (SiO_2 + Al_2O_3 + Fe_2O_3)$, needs to be supplemented by the "Clay index," *i.e.*, the ratio $SiO_2 : (Al_2O_3 + Fe_2O_3)$, in order to serve as a criterion of the rational composition of a Portland cement. For mixtures in which the hydraulic modulus ranges between 1·8 and 2, the most favourable results as regards clinker formation in a rotary kiln are given by mixtures with a clay index between 2·5 and 3. From theoretical considerations, confirmed by practical trials, it is concluded that with hydraulic modulus between 1·8 and 2·2 the most advantageous equilibrium between the four essential constituents of Portland cement is represented by the expression

$$\frac{SiO_2}{Al_2O_3 + Fe_2O_3} = -2{\cdot}5\,\frac{CaO}{SiO_2 + Al_2O_3 + Fe_2O_3} + 7{\cdot}5$$

High Pressure Steam Test for Cement.

The high pressure steam test for soundness of Portland cement has been the subject of investigation by Wig and Davis,[57] who found no evidence that under normal conditions of construction this comparatively rapid test is of value for determining the ultimate soundness of concrete, though it may be of value as forecasting the behaviour of neat cement or a very rich mortar when exposed under normal conditions in dry air.

Standard Specifications for Cement.

Attention may be directed to the British Standard Specification for Portland cement issued by the Engineering Standards Committee,[58] and also to the American Standard Specifications for cement.[59]

Data for Hydraulic Cements.

H. Burchartz[60] reports the results of physical and mechanical tests, and of chemical analysis, of numerous cements of various types, with certain mean results and values, and the limits and mean percentages of the various constituents in the different classes of hydraulic cements.

Some Special Hydraulic Cements.

A special hydraulic cement suitable for constructions in sea water or water containing sulphates has been prepared by A. Klein.[61] The

[56] *Annali Chim. Appl.*, 1915, **4**, 329; *J.*, 1916, 179.
[57] *J. Franklin Inst.*, 1915, **179**, 577; *J.*, 1915, 614. [58] *J.*, 1915, 615.
[59] *Year Book of Amer. Soc. Testing Materials*, 1914, 290; *J.*, 1915, 31.
[60] *Mitt. Königl. Materialprüfungsamt*, 1915, **33**, 29, 34; *J.*, 1915, 963. See also *J.*, 1909, 1250; 1912, 818. [61] Fr. Pat. 472619, 1914, *J.*, 1915, 494.

cement clinker is ground with 5–20 % of an anhydrous oxide of magnesium, copper, iron, tin, lead, aluminium, nickel, or zinc, preferably with 10 % of iron oxide. Gresly's cement[62] for similar purposes is prepared by adding gypsum, as sintering agent, to calcium silicate, siliceous limestone, or a mixture of calcium carbonate (or quicklime) with silica, and the sintered product is pulverized as usual.

Van der Toorn[63] claims that titaniferous sand mixed with cement and sand yields a product with high specific gravity and great resistance to compression, and that when mixed with water it sets quickly.

Permeability of Concrete.

In testing for permeability numerous specimens of concrete composed of Portland cement, pit sand, and gravel in certain specified proportions, M. O. Withey[64] found that permeability decreased rapidly with the age of the specimens for the first month, after which the change was slight. In order to produce good concrete, it was found to be important to grade the sand and gravel into different sizes, and to recombine these so as to obtain the maximum density. Most of the more impervious mixtures used in the tests contained 40–46 % of fine material, and impermeability generally increased with density.

Reports on Testing Cements, etc.

Very brief references must suffice for reports on the testing of cements, mortars, and concretes, including Williams[65] on the time of setting of cements, Wig, Williams, and Gates[66] on the compressive strength of Portland cement mortars and concretes, M'Daniel[67] on the influence of temperature on the strength of concrete, Gary[68] on testing of plastic mortars, Burchartz[69] on tests of concretes and the sand strength of cements, Hattori[70] on the time of setting of cement, Rodt[71] on the behaviour of Portland cement mortars in different salt solutions, and Emley and Young[72] on the strength of lime mortar. As regards the tests of concretes, it may be mentioned that Burchartz[73] states that for

[62] Eng. Pat. 8551, 1915, *J.*, 1916, 180.
[63] Eng. Pat. 13081, 1915, *J.*, 1916, 424.
[64] *Western Soc. Engineers* (*U.S.A.*), 1914; *Engineering*, 1915, **99**, 589; *J.*, 1915, 662.
[65] *J.*, 1915, 30.
[66] *J. Franklin Inst.*, 1915, **180**, 608; *J.*, 1916, 1251.
[67] *J. Gas Lighting*, 1915, **122**, 439; *J.*, 1915, 1252.
[68] *Mitt. k. Materialprüfungsamt*, 1914, **32**, 434; *J.*, 1915, 1251.
[69] *Ibid.*, 1914, **32**, 474, and 1915, **33**, 113; *J.*, 1915, 1251, and 1916, 117.
[70] *J. Chem. Ind., Tokyo*, 1915, **18**, 1189; *J.*, 1916, 117.
[71] *Mitt. k. Materialprüfungsamt*, 1915, **33**, 229; *J.*, 1916, 541.
[72] *J.*, 1915, 30.
[73] *Mitt. k. Materialprüf.*, **32**, 474; *J.*, 1915, 1251.

practical purposes the figures obtained may be used for calculating the strength of different concrete mixtures from results obtained with one mixture of the same materials, and for calculating the strength after 28 days from the strength after 7 days.

Some Cementitious Building Materials.

A building material of a cementitious nature is prepared, according to Rudiger,[74] from a mixture of magnesia, magnesium sulphate, kieselguhr, and trass, with filling materials which do not putrefy or smell. It sets to a stone-like material which is resistant to water, and even with iron reinforcement the product is said to be lighter than water.

Schumann[75] states that an excellent mortar, which hardens in 24 hours, is obtained by mixing waste carbide sludge (from the manufacture of acetylene) with 40 % of sand.

Alkaline By-products in Cement Manufacture.

The present exceptional circumstances give special interest to possible sources of alkali, so some of the following processes may not be unworthy of a little attention. In Newberry's process[76] for recovering alkalis from cement kilns, the stack-gases, after separation of flue dust, are cooled and washed with water. Various methods have been devised for the extraction of potash from felspar and other siliceous minerals, usually in association with the production of cement. In Jungner's method,[77] lime or calcium carbonate is heated with the felspar, etc., preferably in the proportion of one part of felspar to about three parts of calcium carbonate; rapid and complete volatilization of the oxides of potassium and sodium occurs at 1400°–1450° C., the residual cement clinker containing very little alkali. When Jungner's method is applied to the ordinary process of cement manufacture, the potassium oxide is converted into carbonate, which condenses as a fine white powder. R. van der Leeden[78] heats natural double silicates with calcium chloride (or a waste product containing this), and with a small quantity of a reducing agent (such as carbon). H. E. Brown[79] melts a mixture of felspar or similar natural silicate, with a calcium compound (preferably the carbonate) in a non-reducing or oxidizing flame, when the alkali is

[74] Ger. Pat. 292104, 1914, *J.*, 1916, 843.

[75] *Chem.-Zeit.*, 1915, **39**, 43; *J.*, 1915, 231.

[76] U.S. Pat. 1150295, 1915, *J.*, 1915, 963. See also U.S. Pat. 1121532, 1914, *J.*, 1915, 179.

[77] *St-in v. Cement*, 1914; *Chem.-Zeit.*, 1915, **39**, Rep., 63; *J.*, 1915, 421.

[78] Ger. Pat. 281006, 1914, *J.*, 1915, 492 and 494.

[79] Fr. Pat. 473279, 1914, *J.*, 1915, 553. See also U.S. Pat. 1124238, 1915, *J.*, 1915, 179.

volatilized, and the residue is afterwards converted into cement; part of the calcium carbonate in the first stage may be replaced by sufficient calcium chloride to react with the alkali. A. W. Heyman[80] heats (preferably above a red heat) mineral containing insoluble alkali with a suitable proportion of calcareous material, the product being lixiviated with water to remove alkali, and the insoluble residue employed for making cement. C. Ellis[81] fuses at about 1300° C. a mixture of siliceous material containing potassium with calcareous material and calcium chloride; potassium chloride is volatilized and collected, and the non-volatile residue is converted into a hydraulic cement.

It may be added that C. G. Cresswell[82] reviews the whole question of possible sources of potash.

Plaster of Paris.

E. Canals[83] states that sodium and magnesium sulphates are nearly always present in traces in plaster of Paris, mostly in about equal proportions. They materially reduce the time required for the plaster to set, sodium sulphate having a stronger effect than magnesium sulphate in this respect.

To produce gypsum cement, A. Denny and D. G. Anderson[84] completely dehydrate rock gypsum by calcination, and grind it with from 1 to 10 % of its weight of Portland cement, or of ferrous sulphate, etc. The product (containing Portland cement) is intended more especially for use, with suitable filling material, as a composition for the decks of ships.

Rohland,[85] in discussing the hydration of the hemihydrate of calcium sulphate, remarks that whilst colloids retard the velocity of hydration, many electrolytes either retard or accelerate it according to their concentration. An increase in solubility (produced for example by the formation of a complex ion, as in the case of NaCl, KCl, KBr, NH_4Cl, $MgCl_2$, $NaNO_3$, etc.), is accompanied by an increased rate of hydration of the calcium sulphate, since the less soluble dihydrate crystallizes out, and more hemihydrate dissolves. Calcium salts, soluble sulphates, alcohol, etc., decrease the solubility and retard the hydration, unless other effects, at greater concentrations, mask the effects of the mass action law, as in the case of the sulphates. Thus sodium, potassium, and magnesium sulphates in small concentration retard hydration, but

[80] U.S. Pats. 1160171 and 1160172, 1915, *J.*, 1915, 1250 and 1252.
[81] U.S. Pat. 1186522, 1916, *J.*, 1916, 843. [82] *J.*, 1915, 387.
[83] *J. Pharm. Chim.*, 1915, **11**, 286; *J.*, 1915, 717.
[84] Eng. Pat. 21987, 1914, *J.*, 1915, 1146. Also Eng. Pat. 16560, 1914, *J.*, 1915, 836. [85] *Z. anorg. Chem.*, 1914, **89**, 352; *J.*, 1916, 82.

at greater concentration they accelerate it, as does also sulphuric acid (which forms the HSO_4 ion). The water-soluble extract of bean straw has been proposed[86] as a retarding agent to be mixed with the mortar and water of gypsum plaster. While mucilaginous substances retard the setting of plaster, alum and common salt accelerate it.[87]

In discussing the effects of foreign substances on plaster of Paris, Troxell[88] states that adhesive materials (which are often mixed with plaster) do not as a rule strengthen it; dextrin, gum arabic, and glue weaken it, but shellac strengthens the surface to which it is applied; water-glass also weakens plaster.

[86] U.S. Pat. 1151095, 1915, *J.*, 1915, 1011.
[87] *J. Pharm. Chim.*, 1914, **9**, 5; *J.*, 1914, 1089.
[88] *Amer. J. Sci.*, 1915, **41**, 198; *J.*, 1916, 310.

OILS, FATS, AND WAXES.

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The amount of original work on oils and fats published during the period under review has been somewhat meagre, although the war has given a great impetus to the edible fat industry and also, in a lesser degreee, to the production of lanolin and lubricating greases.

Manufacturers in general seem to be more reticent concerning the details of their processes, and also more chary of resorting to the Patent Office, preferring, no doubt, to work any new processes in secret until it can be ascertained how the Patent Laws will be affected at the close of the war.

General.

J. J. Cerdeiras[1] claims to have isolated from cod-liver oil the glyceride of tetrachlorotetraiodotherapic acid, $C_3H_5(C_{17}H_{25}O_2Cl_4I_4)_3$. A good deal of doubt has been thrown upon the existence in natural oils and fats of fatty acids containing an uneven number of carbon atoms, but it must be admitted that strong evidence is being adduced of the presence of these bodies.

The tetrachlorotetraiodo derivative of the hitherto considered hypothetical therapic acid was also prepared by Heiduschka and Rheinberger.[2]

Of great interest to the consideration of the amount of unsaponifiable matter in cod-liver oil is the work of M. Tsujimoto,[3] who has found in the oil obtained from the liver of a variety of Japanese shark (*Squalus mitsukurii*) 90 % of hydrocarbons, chiefly consisting of $C_{30}H_{50}$. Small amounts of hydrocarbons have previously been known to exist in the unsaponifiable matter contained in liver oils, but the bulk of this unsaponifiable matter was considered to consist chiefly of bodies of an alcoholic nature—cholesterol in the case of cod-liver oil and cetyl alcohol in the case of shark-liver oil.

[1] *Anal. Fis. Quim.*, 1915, **13**, 439; *J.*, 1916, 477.
[2] *Pharm. Zentralb.*, 1911, 32.
[3] *J. Chem. Ind. Tokyo*, 1916, **19**, 277; *J.*, 1916, 609.

In view of the somewhat high amounts of unsaponifiable matter occasionally found in Japanese cod-liver oils, it would be interesting to know whether this large amount of hydrocarbons is a normal constituent of the liver of the *Squalus mitsukurii* or whether it exists only at a particular stage in the career of the fish, or perhaps is a product of disease. The hydrocarbon $C_{30}H_{50}$ is a colourless oil having a specific gravity at 15° C. of 0·8587, and possessing strong drying properties. It yields a bromide, $C_{30}H_{50}Br_{12}$.

According to H. Mastbaum,[4] the oils from the livers of *Centrophorus granulosus* and *Scymnus lichia* also contain large amounts of unsaponifiable matter. The liver oils from these two species had the following characteristics: sp. gr. at 15° C., 0·8637, 0·8711; butyrorefractometer at 25° C., 102, 93; optical rotation in 200 mm. tube, −0·3, −2·33; saponification value, 15·4, 36·7. In view of the fact that 70 % of the unsaponifiable matter distilled between 205° and 330° C., the major portion of it consists probably of hydrocarbons. The optical rotation shows that the proportion of cholesterol must be low.

R. F. Ruttan and M. T. Marshall[5] have examined a specimen of adipocere. They give the composition: palmitic acid, 67·52 %; stearic acid, 3·3 %; oleic acid, 5·24 %; *i*-hydroxystearic acid, 9·48 %; κ-hydroxystearic acid, 6·32 %; glycerides, 1·37 %; unsaponifiable matter, 0·87 %; lime soaps, 4·41 %. No indication of the probable origin of the substance is given. The amount of unsaponifiable matter appears to be very low.

B. H. Nicolet and L. M. Liddle[6] have detected azelaic acid in a sample of fuller's earth which had been used for refining cottonseed oil, and had been kept in contact with air for eighteen months. About 95 % of the acid was combined, which supports the modern theory of rancidity as being due more to oxidation than to hydrolysis.

A. Kronstein[7] has published a paper on the mesomorphic polymerization of oils, in which he shows that by stopping the heating of the oil before it has become jellified a solid polymer can be isolated from the still liquid oil. It is said that by removing the non-polymerizable constituents all oils will gelatinize in a similar manner to tung oil.

The amount of non-polymerizable substances removed by distillation *in vacuo* before the oil sets to a jelly is characteristic for each oil, and the following numbers are given: tung oil, 0 %; linseed oil, 19·2 %; perilla oil, 18·5 %; hempseed oil, 20·5 %; walnut oil, 24 %; poppy-

[4] *Chem.-Zeit.*, 1915, **39**, 889; *J.*, 1916, 316.
[5] *Proc. Amer. Soc. Biol. Chem.*, Dec., 1915, 12; *J.*, 1916, 47.
[6] *J. Ind. Eng. Chem.*, 1916, **8**, 416; *J.*, 1916, 696.
[7] *Ber.*, 1916, **49**, 722; *J.*, 1916, 608.

seed oil, 25 %; sunflowerseed oil, 25 %; soya bean oil, 25·4 %; almond oil, 33 %; castor oil, 48 %; cottonseed oil, 33·6 %; maize oil, 35·5 %; rape oil, 35·6 %; sesamé oil, 42·5 %; arachis oil, 53 %; olive oil, 54 %.

The polymerization of tung oil has also been studied by C. L. Schumann.[8]

A. H. Salway[9] shows that, when linolenic acid is oxidized, acrolein is found among the volatile products in quantities of about 0·3 to 0·5 %. He points out that this fact cannot be explained by Erdmann and Bedford's formula for the stereoisomeric linolenic acids.

A. Grün and H. Schönfeld[10] have prepared pure glycerides of linolic acid. The diglyceride was prepared by the action of $\alpha\alpha$-dichlorohydrin on the potassium salt of linolic acid tetrabromide, and the bromine subsequently removed by a solution of potassium iodide in ethyl acetoacetate. Mixed glycerides were synthesized by heating diglycerides with a linolic anhydride; α-linolo-$\alpha'\beta$-distearin melts at 33·5° to 34° C.; β-linolo-$\alpha\alpha'$-distearin melts at 41°–42° C.; α-linolo-$\alpha'\beta$-dipalmitin melts at 11·5°–13° C.; and β-linolo-$\alpha\alpha'$-dipalmitin at 28°–29° C.

E. Anderson and H. L. Brown[11] have published an interesting paper on the velocity of saponification of oils and fats. Their conclusions may be given briefly. Very slight differences were observed in the different oils and fats; butter fat, as might be expected, was saponified more rapidly than cottonseed oil.

The choice of a solvent was of importance, as it was found that the velocity in amyl alcohol was double that in ethyl alcohol, and in ethyl alcohol saponification takes place in one-tenth of the time required for methyl alcohol.

A. E. Dunstan[12] has published the viscosities of some saturated fatty acids at 70°, 80°, and 90° C. Lauric acid at these temperatures yielded the values 4430, 3620, 2990; myristic acid, 5835, 4645, 3810; palmitic acid, 7835, 6130, 5000; stearic acid, 9870, 7720, 6098.

Le Sueur and Withers[13] have prepared heneicosoic acid, $CH_3(CH_2)_{19}COOH$, by the reduction of α-ketoheneicosoic acid with amalgamated zinc and boiling hydrochloric acid. Its melting-point was 73°–74° C., while the melting-points of its α-bromo- and α-hydroxy-derivatives were 65·5°–66·6° C. and 93°–94° C. respectively.

[8] *J. Ind. Eng. Chem.*, 1916, **8**, 5; *J.*, 1916, 548.
[9] *Chem. Soc. Trans.*, 1916, **109**, 138; *J.*, 1916, 366.
[10] *Z. angew. Chem.*, 1916, **29**, 37, 46; *J.*, 1916, 366.
[11] *J. Phys. Chem.*, 1916, **20**, 195; *J.*, 1916, 478.
[12] *Chem. Soc. Trans.*, 1915, **107**, 667; *J.*, 1915, 722.
[13] *Ibid.*, 1915, **107**, 736; *J.*, 1915, 804.

J. Klimont and K. Mayer[14] have isolated a glyceride melting at 59°–60° C. by the repeated recrystallization of goose fat. The fatty acids are stated to consist chiefly of margaric acid and palmitic acid, and these observers assume it to be a dipalmito-margarine. Since, however, the margaric acid prepared from lard has been found to be an eutectic mixture of stearic and palmitic acids, this statement must be accepted with reserve.

A. Windaus and C. Resau[15] show that, by the oxidation of cholesteryl acetate, β-oxycholestenol ($C_{27}H_{44}O_2$) is formed. The ketone prepared from this body, oxycholesterylene ($C_{27}H_{42}O$), when reduced by sodium and alcohol, yields pseudocholesterol ($C_{27}H_{46}O$), of m.pt. 116° C. and isomeric with cholesterol.

Marcusson and Meyerheim[16] have studied the effect of the catalytic reduction of oils and fats on the characteristics of the unsaponifiable matter. Their results seem to show that, although no derivatives of cholesterol can be isolated, its quantity was diminished. The unsaponifiable matter from vegetable oils, on the other hand, yielded an alcohol melting at 75° C., which did not give the sitosterol reaction.

It is not stated whether unchanged sitosterol was also present, and its conversion into a saturated alcohol requires confirmation. It is interesting to note in this paper that the rotation of the unsaponifiable matter of sesamé oil is increased to $[\alpha]_D = 102°$ when the sitosterol is removed by the digitonin method.

E. Erdmann[17] states that the hydrogenation of oils proceeds differently according to whether nickel oxide or nickel itself is used as catalyst. He brings forward some fresh evidence in support of his view that in the process of catalytic hydrogenation it is unnecessary for the nickel oxide to be reduced to metallic nickel, but the question is still left in considerable doubt.

New Oils and Fats.

The high prices ruling for oils and fats is stimulating the search for new oil-bearing nuts and seeds, more especially those suitable for edible purposes for the margarine maker, etc.

The chief difficulty in their commercial exploitation is the cost of their collection and conveyance to a port, and also at the present time the difficulty of obtaining steamer space.

[14] *Monatsh. Chem.*, 1915, **36**, 281; *J.*, 1915, 878.
[15] *Ber.*, 1915, **48**, 851; *J.*, 1915, 850.
[16] *Mitt. K. Materialprüf.*, 1916, **33**, 221; *J.*, 1916, 549.
[17] *J. prakt. Chem.*, 1915, **91**, 469; *J.*, 1915, 969.

E. R. Bolton and E. M. Jesson[18] describe a number of little known oil seeds, among which may be noticed Marquaqua or M'Quaqua nuts which yielded 20 % of a dark yellow oil solidifying at 40° C., and having the saponification value 189·3 ; iodine value 70·1, and containing 1·26 % of unsaponifiable matter.

G. Kassner and K. Eckelmann[19] have examined the oil from the kernels of plum stones, *Prunus domestica*, and find that they contain 42·9 % of a pale yellow oil resembling in taste almond oil, and having the following characteristics :—sp. gr. 0·916 ; saponification value 188·1 : and iodine value 104.

Barnes and Arjan Singh[20] have examined the oil from the wild safflower, *Carthamus oxyacantha*. The oil is stated by these observers to be termed by the natives poli oil, and to be used as an adulterant of ghi. It would seem to be a most unsuitable oil for the purpose, as it has strong drying properties and a most pronounced taste. The characteristics given simulate those of the cultivated safflower, *Carthamus tinctorus*, with the exception of the acetyl value, which is stated to be 60·5 as against 11·16 for the true safflower. This abnormal figure requires further confirmation.

H. Wagner and J. B. Lampart[21] state that the seeds of *Canarium polyphyllum* yielded 69·58 % of a buttery fat having sp. gr. at 30° C. 0·9042 ; m.-pt. 22° C. ; solidifying point 10 to 9° C. ; saponification value 189·7 ; iodine value 52·95 ; Reichert-Meissl value 0·33 ; titration number of the insoluble volatile acids 0·4 ; butyrorefractometer reading at 40° C. 47·4. These figures do not confirm the analysis published by M. Krause,[22] but are probably more worthy of credence, since Krause states that the saponification value of the oil is 200·2, while the Reichert-Meissl value was 4·41.

These observers have also examined the oil from *Coula edulis* from the Cameroons and *Limonia warneckei* from Togo.[23]

[18] *Analyst*, 1915, **40**, 3 ; *J.*, 1915, 143.

[19] *Arch. Pharm.*, 1914, **252**, 402 ; *Chem.-Zeit.*, 1915, **39**, Rep. 165 ; *J.*, 1915, 668.

[20] *Analyst*, 1916, **41**, 72 ; *J.*, 1916, 428.

[21] *Z. Unters. Nahr. Genussm.*, 1915, **29**, 105 ; *J.*, 1915, 722.

[22] *Der Tropenpflanzer*, 1913 (7), 147.

[23] *Z. Unters. Nahr. Genussm.*, 1915, **30**, No. 6, *Bull. Agric. Intell.*, 1915, **6**, 1634 ; *J.*, 1916, 367.

The oils had the following characteristics :—

—	*Coula edulis.*	*Limonia warneckei* (*Afraegle paniculata*).
Yield of fat	30·48%	38·5%
Sp. gr. at 25° C.	0·9116	—
Butyrorefractometer at 40° C.	51·2	47·7
Free fatty acids	9·2%	3·6%
Saponification value	189·7	188·8
Iodine value	83·36	75·2
Reichert-Meissl value	0·38	0·55
Melting point...	—	32·4° C.

The seeds of *Marytynia Louisiana*, a weed growing in great abundance in the Southern States of America, contain, according to E. H. Bailey and W. S. Long,[24] 60·8 % of an oil resembling olive oil, and having the following characteristics :—Specific gravity 0·9157 ; saponification value 197·1 ; iodine value 122·5 ; refractive index at 15·5° C. 1·4767.

The oil from the seeds of *Monodora myristica* ("Owere" seed)[25] showed the following characteristics :—sp. gr. at 15° C. 0·918 ; saponification value 180·6 to 186·7 ; iodine value 110·6 to 118·4 ; unsaponifiable matter 1·6 %. The oil was dark brown in colour and amounted to 35 % of the seed.

The oil from the seeds of the wild grape, *Vitis riparia*, has been examined by G. D. Beal and C. K. Beebe.[26] The seeds yielded to petroleum spirit 19·4 % of oil which is described as having a taste similar to castor oil. The following characteristics were determined :—sp. gr. at 15° C. 0·9425 ; refractive index 1·4781 ; saponification value 187·8 ; iodine value 76·5 ; acetyl value 61·3 ; insoluble fatty acids 90 %. The insoluble fatty acids were separated into 95 % of liquid acids having an iodine value 92 and 5 % of solid acids. The solid acids are stated to consist of 64 % of palmitic acid and 36 % of stearic acid, while the liquid acids contain 44 % of oleic and ricinoleic acids and 56 % of linolic acid. This large amount of linolic acid does not agree with the low iodine value.

A number of Japanese oils have been examined by S. Higuchi,[27] among which may be noticed the oil from Yabunikkei seeds, which has an

[24] *Oil, Paint, and Drug. Rep.*, July 5, 1915 ; *J.*, 1915, 804.
[25] *Bull. Imp. Inst.*, 1915, 346 ; *J.*, 1915, 1224.
[26] *Journ. Ind. Eng. Chem.*, 1915, **7**, 1054 ; *J.*, 1916, 126.
[27] *Bull. Forest Expt. Stat., Meguro, Tokyo*, 1915 ; *J.*, 1916, 261.

unusual composition, inasmuch as the saponification value is 276·9, while the Reichert-Meissl value is only 1·30. It will be interesting to know the titration number of the insoluble volatile acids. The mean mol. wt. of the fatty acids was 196·6. The oil most probably consists of the glyceride of lauric acid.

C. A. Jacobson and A. Holmes[28] have isolated from alfalfa seeds 9·47 % of a drying oil having the saponification value 172·3 and iodine value 154·2. The high acetyl value of 19·8 is most likely due in a great measure to the large amount of unsaponifiable matter, which was found to be 4·4 per cent. A curious feature of the analysis is that while the free fatty acids are only 1·4 %, the yield of glycerol was 1·97 %. This requires further confirmation. It is stated that the oil contains oleic, linolic, and linolenic acids among the liquid acids and carnaubic, daturic, and behenic acids among the solid acids which amount to 9·6 %.

H. C Brill and F. Agcaoili[29] have examined the oils from the cato nut (*Chisochiton cumingianus*), and pili nuts (*Canarium pachyphyllum*). The cato nut yielded on expression 35·56 % of a non-drying oil having mild purgative properties. It is said to be used in the manufacture of soap in Manila. The kernels of the pili nuts yielded 74·39 % of an edible oil.

The oils have the following characteristics :—

—	Cato nut oil.	Pili nut oil.
Sp. gr. at 15° C.	0·9230	—
Sp. gr. at 30° C.	0·9188	0·9067
Butyrorefractometer at 30° C.	60	54
Saponification value	192·0	192·6
Iodine value	80·78	61·25
Reichert-Meissl value	7·34	3·3

The observed Reichert-Meissl values, particularly in the case of the cato oil, are much higher than is warranted by the saponification value, unless the proportion of the unsaponifiable matter, which has not been determined, is high.

The fruit of the cokerite palm[30] (*Maximiliana regia*) consists of a pericarp thinner than in the case of the palm fruit, enclosing a nut similar to the fruit of the ordinary palm. The pericarp yields 15 % of a soft

[28] *J. Amer. Chem. Soc.*, 1916, **38**, 480; *J.*, 1916, 367.
[29] *Philippine J. Sci.*, 1915, **10A**, 105; *J.*, 1916, 609.
[30] *Bull, Imp. Inst.*, 1916, **14**, 8; *J.*, 1916, 695.

red oil. The kernels yield 56·9 % of a yellowish fat. The characteristics of the two oils are contrasted in the following table :—

	Oil from pericarp.	Oil from kernel.
Melting point	—	27° C.
Free fatty acids	14·3%	1·5%
Sap. value	211·6	253
Iodine value	51·4	13
Solidifying point of fatty acids	25·5° C.	24° C.

Waxes.

Seiichi Ueno[31] has determined the characteristics of a number of Korean beeswaxes and finds that the average figures are as follows :— Sp. gr. (100°/4° C.) 0·8299 ; m. pt. 65·6° C. ; refractive index calculated to 40° C. 1·4580 ; butyrorefractometer calculated to 40° C. 48·0 ; acid value 5·85 ; sap. value 84·56 ; difference 78·71 ; ratio number 13·45 ; iodine value (Wijs) 11·41. It is evident from the low acid value and correspondingly high ratio number that these waxes resemble East Indian beeswaxes in their composition, and it will be interesting to see how they behave in the Weinwurm test.

M. S. Salamon and W. M. Seaber[32] describe a useful method for the detection of small amounts of paraffin wax in beeswaxes, which is more delicate than the Weinwurm test ; this is based on the difference in temperature at which the saponified alcoholic solution becomes turbid. They operate as follows :—1 grm. of the wax is boiled for one hour, with 10 c.c. of $N/2$ alcoholic potash and 10 c.c. of alcohol (no strength given) under a reflux condenser. The flask is disconnected and the contents stirred continuously with a thermometer, the temperature at which the solution becomes cloudy being observed and termed the clouding point. An Indian beeswax with the clouding point of 60° C., on admixture with 5 % of paraffin wax, gave 66° C., and with 10 % paraffin wax 75° C., while an Italian wax with the clouding point of 56° C. gave, after admixture with 5 % paraffin wax, 62° C., and with 10 % paraffin wax, 70° C.

M. S. Salamon[33] has also examined a large number of European, South American, and African beeswaxes, in all of which the ratio number was about normal, and the clouding point varied between 59·5° and 61° C.

[31] *Analyst*, 1915, **40**, 343 ; *J.*, 1915, 913.
[32] *J.*, 1915, 461. [33] *J.*, 1916, 8.

Richardson and Bracewell[34] contribute an interesting paper on the analysis of beeswaxes and wool wax, in which they show the unreliability of Buisines' reaction for the determination of the amount of alcohols in the unsaponifiable portion of an adulterated wax.

C. Budde[35] has prepared on a commercial scale from esparto grass a hard light brown wax melting at 74° C. It had the following characteristics :—Acid value 34·4 ; saponification value 71·4 ; unsaponifiable matter soluble in hot carbon tetrachloride 50·34 % ; fatty acids 45·89 % ; iodine value 6·48.

These figures show that the mean molecular weight of the fatty acids is about 360. These fatty acids evidently contain a large proportion of cerotic and possibly melissic acids.

A. J. Ultée[36] has ascertained that ficoceryl alcohol from gondang wax is identical with β-amyrin.

Three new vegetable waxes are described by Hébert and Heim.[37] The plants bearing them, viz. : *Cynanchum messeri* (*Vohemaria messeri*) Asclep., *Euphorbia xylophylloides*, and *Euphorbia stenoclada*, have been discovered growing wild in the desert regions of Madagascar. They had an extremely high melting point (88° C.), and their acid values ranged from 17·7 to 28, saponification values from 140 to 159·6, and iodine values from 3·2 to 5·9.

Technological.

F. Canzoneri[38] states that olive oils extracted from the marc with carbon bisulphide cannot be bleached by means of sulphur dioxide, ozone, or hydrosulphite. He has, however, found that the use of ultra-violet rays and also treatment of the oil with potassium chromate and sulphuric acid causes a considerable improvement in the colour. As would be expected, he finds that the presence of considerable amounts of free fatty acids increases the difficulty of bleaching the oil, and recommends, therefore, in cases where the oil contains more than 50 % of free fatty acids, to deacidify by treatment with lime and subsequent extraction of the neutral oil with a volatile solvent.

This does not appear at first glance to be a very promising process, as a similar process tried some years ago by the writer resulted in quantities of the lime soap passing into the solvent (petroleum ether), causing the neutral oil to set to a jelly when the solvent was driven off.

[34] *J.*, 1916, 160. [35] *J.*, 1916, 401.

[36] *Pharm. Weekblad*, 1915, **52**, 1097 ; *J.*, 1915, 1061.

[37] *Bull. de l'Office Colonial*, 1915, **8**, 96 ; *Bull. Agric. Intell.*, 1915, **6**, 831 ; *J.*, 1915, 1061.

[38] *Annali Chim. Appl.*, 1915, **3**, 344 ; *J.*, 1915, 840.

More hopeful is a method due to the same author of converting the free fatty acids into their ethyl esters. Such a product prepared from an olive oil had the following composition: Esters of non-volatile fatty acids, 51 %; esters of volatile fatty acids, 2 %; glycerides, 37 %; free fatty acids, 5 %; hydroxystearic acid, 3 %; and stearolactone, 2 %.

S. Ueno[39] has continued his work on the bleaching action of Kambara earth, and shows that the best results are obtained at a temperature below 140° C. A curious colour reaction may be noticed, a bluish-green colour being produced when cod-liver oil is shaken with the earth.

S. G. Sastry[40] recommends for bleaching palm oil the use of a current of air in the presence of the borates of manganese and cobalt as catalysts. Since, however, soft palm oils are easily bleached by means of air alone, it is difficult to see the need of a catalyst. The author does not state the origin of the palm oil, but presumably it was a soft or medium oil.

An important paper by the same author[41] on the action of chlorinated hydrocarbons on metals in the presence of moisture and oil seeds has been published, wherein it is shown that di- and trichloroethylenes are the safest to use. It must be borne in mind that a slight action on the metal may cause discoloration of the extracted oil, and the writer has always found oils extracted by means of trichloroethylene more difficult to bleach than oils extracted with petroleum ether. This is due in part to the solvent action which the trichloroethylene exerts on the colouring matters contained in the kernels.

C. K. Keutgen[42] proposes to deodorize the fatty acids from fish oils by treating them with concentrated sulphuric acid, and subsequently boiling with water, in order to convert the sulphonated fatty acids into hydroxy-acids before distillation. It would appear simpler to hydrolyze the oil itself by treatment with concentrated sulphuric acid, as is done in the case of tallow for candle-making. A further method is given by which it is claimed that odourless neutral fats may be prepared. It consists in driving off the volatile substance by means of a current of carbon dioxide passed through the oil heated to between 125° and 250° C. The residual oils, however, as will be expected, simulate polymerized oils in their appearance.

A method of refining oils by means of caustic soda, which does away with the necessity for allowing the soap sludge to settle, and consequently shortens the time required for the operation, has been devised

[39] *J. Ind. Eng. Chem.*, 1915, **7**, 596; *J.*, 1915, 840.
[40] *Chem. Soc. Trans.*, 1915, **107**, 1828; *J.*, 1916, 126.
[41] *J.*, 1916, 94.
[42] *Seifensiederzeit.*, 1915, **42**, 552, 573, 594, 617; *J.*, 1916, 186.

by C. Baskerville.[43] This method consists of treating the oil with caustic soda together with 2 % of prepared cellulose, which is stirred into the oil while it is being heated to 45°–60° C. The cellulose and soap may then be removed in a filter-press.

R. Seligman and P. Williams[44] have studied the action of the lower fatty acids on aluminium at their boiling-points. It is noteworthy that anhydrous acids corrode the metal much more rapidly than acids of 99 % concentration. They also show that with the higher fatty acids no action takes place below 270° C. It is important for the oil-refiner to know if any corrosion occurs in the presence of traces of soap, and using superheated steam under such conditions as occur in the refining of edible oils.

Analysis.

A rapid method for the determination of boric acid in butter is described by Hawley,[45] which depends on the depth of colour produced by the addition of an infusion of turmeric compared with a solution of boric acid of known strength.

H. J. Cranfield[46] suggests the relationship between the difference of the Reichert-Meissl and Kirschner values and the Polenske value as giving more accurate results in the analysis of butter than by the Reichert-Meissl value and Polenske value when taken alone. Figures are given in the original paper for a large number of pure butters, which to some extent bear out the author's contention, as they lie within narrower limits than do the figures given by Polenske, but the method must be used with great circumspection, as a slightly abnormal butter may be looked upon as adulterated if the figures given are followed too rigidly.

A rapid method for the determination of fat in powders which should prove of great use to the works chemist is due to S. B. Phillips.[47] It consists, in short, in shaking the powder with a known volume of trichloroethylene and weighing the fat derived from an aliquot portion of the solvent. An ingenious method for filtering and measuring off the solvent is given in the paper, as also is a table of factors for the increase of volume of the solvent due to the presence of fat, which should, however, be determined by each observer for himself.

C. E. Sage[48] states that the colour obtained in the Baudouin test

[43] *J. Ind. Eng. Chem.*, 1916, **8**, 118; *J.*, 1916, 477.
[44] *J.*, 1916, 88.
[45] *Analyst*, 1915, **40**, 150; *J.*, 1915, 507.
[46] *Ibid.*, 1915, **40**, 339; *J.*, 1915, 1109.
[47] *Ibid.*, 1916, **41**, 122; *J.*, 1916, 642.
[48] *Pharm. J.*, 1915, **94**, 128; *J.*, 1915, 184.

with Tunis and Spanish olive oils changes to lilac within one hour and is quite distinctive from the colour obtained with oils containing sesamé oil.

R. Meldrum[49] finds the melting-point of spermaceti by means of the thermometer bulb method to be 45·3° C., by the open capillary tube method 45·1°–45·4° C., by the closed capillary tube method 45·9°–46° C. and titer test 45·75° C. These figures are closely concordant, as is usually found with the wax. He further states that rapid melting and cooling of the wax has no influence on the melting-point.

To the same observer[50] is due the determination of the solid glycerides crystallized from an ethereal solution of mutton tallow. The solidifying point was determined by Dalican's method, and found to be 49·7°–50·3° C., with a rise of 3·4°–4·6° C.

F. Prall[51] recommends for the detection of nickel in hardened fats by the dimethylglyoxime test the incineration of the fat and subsequent solution of the ash in hydrochloric acid. Some oils which were free from nickel on shaking with hydrochloric acid yielded an acid solution which gave a coloration with this test. This observation can be confirmed by the writer, notably in the case of some vegetable oils.

A. Heiduschka and R. Wallenreuter[52] have isolated from the unsaponifiable matter of *Nux vomica* fat a sitosterol melting at 158° C. and an alcohol melting at 188° C., and having $\alpha_D^{15} = 90°$. The acetate from this alcohol melted at 223° C., and had $\alpha_D^{15} = 74·47°$. These figures confirm the previous results obtained by the same authors.

F. Erban[53] has prepared Turkey-red oil from castor oil fatty acids and contrasted it with the Turkey-red oil prepared from the glycerides. He finds, as was well known, that the Turkey-red oil prepared from fatty acids has less emulsifying power than that prepared from the glycerides.

A. T. Bosch[54] describes a new colour test for sesamé oil whereby a green coloration is developed on the addition of 1 c.c. of a mixture of 2 volumes of sulphuric acid and 1 volume of hydrogen peroxide solution to 1 drop of oil dissolved in 1 c.c. of ether, benzine, or chloroform. This test is unlikely to supersede the well-known Baudouin test.

Marcusson[55] shows that the hydrolysis of fats by means of high-

[49] *Chem. News*, 1915, **111**, 37; *J.*, 1915, 184.
[50] *Ibid.*, 1915, **111**, 98; *J.*, 1915, 288.
[51] *Z. angew. Chem.*, 1915, **28**, 40; *J.*, 1915, 237.
[52] *Arch. Pharm.*, 1915, **253**, 202; *J.*, 1915, 1153.
[53] *Seifenfab.*, 1915, **35**, 477, 519, 578, 598; *J.*, 1916, 127.
[54] *Pharm. J.*, 1915, **94**, 321; *J.*, 1915, 288.
[55] *Mitt. K. Materialprüf.*, 1914, **32**, 502; *J.*, 1915, 1259.

pressure steam takes place in three stages, mono- and di-glycerides being formed as intermediate products, thus confirming Lewkowitsch's theory of saponification. He also states that hydrolysis by means of acids and enzymes takes place in the same stages.

W. McD. Mackey[56] publishes a large number of results obtained with the cloth oil tester, which show that heating proceeds more rapidly when glass-wool or slag-wool is used as the absorbent than when cotton-wool is used. From these figures it is also apparent that the presence of free fatty acids causes the oil to become more dangerous.

W. McD. Mackey and H. Ingle[57] have also studied the catalytic effect of metallic soaps on the heating of olive oil in the cloth oil tester. They find that cobalt is the most active, followed in the order named by Mn, Cr, Ni, Pb, and Cu. It is surprising that lead, which is so active an oxygen-carrier in the case of drying oils, should figure so low down in the list.

A further study on these lines might throw some light on the reason why cobalt is so much superior to lead and manganese as a drier in the case of menhaden oil in contradistinction to the vegetable oils, where lead and manganese give the best results.

E. E. Ware[58] bases a method for the detection of adulterants in Chinese wood oil on the difference in the optical dispersion exhibited by Chinese wood oil and other vegetable oils. In the apparatus used by this observer Chinese wood oil showed a dispersion of 269 units, whilst soya bean oil only showed 129 units.

This seems to be a useful method for the works chemist, as a large number of tests can be done in a short time, but it will probably be of little use for the detection of small amounts of tung oil in other oils.

J. W. Marden[59] has devised an elaborate apparatus for the determination of the heat of bromination, the essential part of which consists of a Dewar vacuum mantle. On multiplying the thermal values obtained by 0·846, he obtains numbers in fair agreement with the iodine values, except in the case of tung oil, where a wide difference was observed. This is a somewhat needless refinement of what, at best, can only be used as a rapid sorting test, the iodine value giving far more reliable figures for quantitative purposes.

L. G. Radcliffe and C. W. Palmer[60] contrast the characteristics of the

[56] *J.*, 1915, 595.
[57] *J.*, 1916, 454.
[58] *Journ. Eng. Ind. Chem.*, 1916, **8**, 126; *J.*, 1916, 477.
[59] *Ibid.*, 1916, **8**, 121; *J.*, 1916, 477.
[60] *J.*, 1915, 643.

fatty acids prepared from cod oil before and after treatment with concentrated sulphuric acid, and give the following results:—

Oil.	Fatty acids.	Fatty acids from sulphonated oil.
Specific gravity 0·931 ...	Titer test 22·8	Titer test 25·7.
Acid value 17·6	Neutralization value 194...	Neutralization value 183.
Sap. value 163·3... ...	M.m.w. 289·4	M.m.w. 308·6.
Iodine value 173·7 ...	Iodine value 178	Iodine value 114·4.
	Insoluble bromides 42% ...	Insoluble bromides 11·0%

From the low saponification value of the oil it will be gathered that there must have been present considerable amounts of unsaponifiable matter, which, however, is not borne out by the neutralization value of the fatty acids. As will be expected, the yield of insoluble bromides (wrongly called in the paper hexabromides) has decreased owing to the double linkages taking up hydroxyl. The neutralization value shows that lactones can only have been present in small amounts, and it would be interesting to know their actual quantity, and also the amount of liquid and solid acids, which might throw a little light on the problem of identifying an oil or mixture of oils in Turkey red oil.

F. H. Newington[61] has devised a method for determining the amount of free caustic alkali in soaps without resorting to the troublesome method of filtering absolute alcoholic solutions. The method consists in "salting out" the soap from its solution with sodium sulphate and titrating the free caustic in the solution with $N/10$ sulphuric acid, using silver nitrate as a spot indicator.

The chief advantage of this method is that it may be applied to highly hydrated soaps without previous drying.

Savill and Cox[62] publish comparative tables and graphs comparing the viscosities obtained by means of the Redwood and Ostwald viscosimeters.

As the Ostwald apparatus requires double the time taken by the Redwood, it appears to the writer that the only possible advantage in using it is that the determination may be made on a much smaller quantity of oil than is required by the Redwood apparatus. For this reason it is well to have an authoritative standard of comparison between the two types of apparatus.

[61] *J.*, 1916, 95.
[62] *J.*, 1916, 151.

C. A. Browne[63] states that the acetyl value as determined by Lewkowitsch's modification does not give a correct measure of the hydroxylated acids in the mixed fatty acids owing to the formation of lactones during their preparation, and prefers the original method of Benedikt and Ulzer or a combination of the two. Since, however, it has been shown by Lewkowitsch that the non-hydroxylated fatty acids form anhydrides on boiling with acetic anhydride by the elimination of water from the carboxyl group, the figures found by Benedikt and Ulzer's method will be too high. It is a simple matter to determine the lactones separately, which should in all cases be done.

[63] *J. Ind. Eng. Chem.*, 1915, **7**, 30; *J.*, 1915, 184.

PAINTS, PIGMENTS, VARNISHES, AND RESINS.

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The years 1915 and 1916 are not marked by great progress in the investigation of paints, resins, and varnishes. The demands of the war have diverted the activities of the scientific and practical worker, and most probably in belligerent countries many discoveries have not been published.

The record of progress may be conveniently classified under the following heads :—

1. The properties of drying oils with reference to their utilization for varnishes and paints.
2. The properties of pigments comprising durability, etc.
3. The properties of natural resins, colophony, and ester gums.
4. Progress in the manufacture of synthetic resins.
5. Cellulose varnishes, including dopes.
6. New work on turpentine.
7. The methods of testing varnishes and the estimation of their components.

The Properties of Drying Oils.

Contributions to the study of the drying of linseed oil have been made by Fritz,[1] who has shown that the acidity produced by addition of 2 % of linolic acid to a boiled oil accelerated the drying; on the other hand, the addition of 2 % of a strongly alkaline soap to a varnish caused no alteration in rate of drying. The addition of lime favoured the linoxyn formation. The oxidation of linseed oil, using a lead drier, was greater in winter than in summer because of the reduced moisture content of the atmosphere.

Experience would seem to indicate the true drying of linseed oil as a product of two factors—the absorption of oxygen primarily, and, secondly, a polymerization. Unpublished investigation of the writer on the drying of the cerium salts of α-elæostearic acid from Chinese wood

[1] *Chem. Rev. Fett Harz Indust.*, 1915, **22**, 19 and 60; *J.*, 1916, 129.

oil show that after the oxygen absorption of the cerium salt has become constant, the peroxide acid or acids gradually polymerize on standing with the production of a varnish-like film.

The oxygen absorption of linseed oil has been investigated by R. W. Darner,[2] who finds that all pure varieties of linseed oil dry in the same time when air is drawn through at the rate of $\frac{1}{2}$ litre per minute at 0·5°–25° C., and by this means 10 % adulteration of the oil can be detected. The same author states that Elsdon and Hawley's method for the detection of soya bean oil gave uncertain results.

Reference must be made to the excellent standard specifications of raw linseed, boiled linseed, and Chinese wood oils which appear in the Year Book of the American Society of Testing Materials.[3] A similar publication would be a boon in England.

De Waele[4] considers that in the oxidation of linseed oil and acids polymerized or resinified acid residues are produced, and in support of this states that in the manufacture of linoleum not more than 50 % of oxidized acids is obtained, together with 25 % of water-soluble acids, corresponding to lower acids resulting from the peroxide decomposition. His conclusions are that direct oxidation gives rise to unstable peroxides, which decompose gradually to form volatile products, and when the oxidation proceeds under conditions favourable to further decomposition, a great absorption of oxygen ensues owing to the disruption of the peroxides. The drying properties of linseed oil treated with lead oxide or with the elæostearates of lead manganese or cobalt have been studied by L. E. Wise and R. A. Duncan,[5] and the rate of drying was compared by determining the increase in weight of the oil against time. The maximum gain in weight was not the same in all cases, but on the whole the rates of drying were nearly the same, and independent of the acid radicle in the drier. The curves showing the increase in weight with the time were similar for the three metals.

By way of criticism it is suggested that for practical purposes a better standard of drying ought to be selected, and that the oxygen absorption or gain in weight is not sufficient in view of the polymerization factor referred to above.

R. S. Morrell[6] has investigated the changes occurring when linseed, tung, poppyseed, and olive oils are heated out of contact with the air.

[2] *N. Dakota Sta. Spec. Bull.* (1914), **2**, No. 21, 367; **3**, No. 1, 8.
[3] *Amer. Soc. Testing Materials*, 1915, 417–27.
[4] *Chem. World*, 1914, **3**, 300.
[5] *J. Ind. Eng. Chem.*, 1915, **7**, 202; *J.*, 1915, 435.
[6] *J.*, 1915, **34**, 105.

His conclusions from the experimental data may be summarized as follows :—

Thickening by polymerization, without change in chemical composition, occurs when there are at least two pairs of doubly-linked carbon atoms in the molecules of the acids of the glycerides. The thickening is due to polymerization of the mixed glycerides, and the first stage is the formation of a product insoluble in acetone, which may be a double molecule of linked glycerides in the case of linseed oil or a quadruple molecule in poppy-seed oil. The change is dependent on the temperature, and an equilibrium is established when 50 % of the modification has been formed. At higher temperatures the final stage is the formation of a polymer insoluble in light petroleum, which seems to be determined in linseed oil by the linolenic acid glyceride.

The linseed oil was heated at 240°–250° C. for twenty-eight to sixty hours, tung oil for twenty minutes, and poppyseed oil at 270°–290° C. for thirty-four hours ; in all three cases the yield of polymerized oil was 50 %. There is evidence in the properties of the salts obtained from the oils (linseed and poppy) soluble in acetone and not polymerized that a shifting of the linkages has occurred. A similar conclusion has been arrived at in the case of tung oil. It is noteworthy that, although the glyceryl esters are polymerized, the methyl esters obtained by Bull's method are in all cases monomolecular.

In connection with the bleaching and thickening of linseed oil, Von Kreybig[7] has investigated the changes in the constants when air is blown into heated linseed oil in the presence of catalysts.

Some interesting work on Chinese wood oil has been done in connection with the problem of coagulation. The uses of sulphur, selenium, and substances readily splitting off a halogen are the subject of several patents.[8] C. J. Schumann[9] has published an investigation on the polymerization of Chinese wood oil, whereby he concludes that the polymerization is analogous to that of linseed oil, and is mesomorphic. An intermediate product soluble in ordinary solvents except light petroleum is admitted, but no reference is made to the modification insoluble in acetone referred to by Morrell,[10] nor to the possibility of isomeric changes in the oil. From unpublished work the writer has shown that the methyl ester of α-elæostearic acid on distillation *in vacuo* undergoes almost complete transformation into the methyl ester of β-elæostearic acid.

[7] *Farbenzeit.*, 1915, **20**, 742.

[8] A. Beringer, Eng. Pat. 21725/1913 ; Ger. Pat. 261403, *J.*, 1913, 834. H. Reissert, Ger. Pat. 274971.

[9] *J. Ind. Eng. Chem.*, 1916, **8**, 5 ; *J.*, 1916, 548.

[10] *J.*, 1915, **34**, 105.

Schumann points out a difference between the properties of elæostearic acid and the polymerized acids whereby a separation is effected. The statement that the addition of lime and lead oxide accelerates the polymerization must not be interpreted too literally, because it is not strictly in keeping with practical experience.

The thickening of fatty oils in the light of mesomorphic polymerization has been investigated further by A. Kronstein.[11] He applies the term "mesomorphic polymerization" to reactions of the type illustrated by the behaviour of fatty oils, which thicken on heating to a jelly. All fatty oils are mixtures of polymerizable and non-polymerizable glycerides. Kronstein gives the "distillation number" of certain fatty oils, which represents the percentage of distillate obtained from the oil before gelatinization commences on heating in a vacuum. The non-drying oils show the highest distillation number, and China wood oil has a zero value. The final product of mesomorphic polymerization cannot be changed into the monomolecular form on further heating, but only into the intermediate form.[12] Chinese wood oil on drying yields a film more resistant to alkali than linseed oil. Fahrion[13] repudiates Kronstein's statement respecting fatty oils being mixtures of polymerizable and non-polymerizable glycerides and that the distillation number is any criterion of their drying properties. He states that no proof is given that the "gelatins" of other oils behave as regards depolymerization in the same manner as Chinese wood oil.

The cultivation of tung oil in the Southern States of America is increasing. In 1914, 40,000 trees were in cultivation,[14] and the oil from American-grown nuts is very similar to that from Chinese nuts.[15] Krumbham[16] has described the modern methods of using Chinese wood oil. Linoxyn and the German linoleum industry are reviewed and discussed by Fritz,[17] and with Clara Zymandi[18] the analytical data of varieties of linoxyn are given. There has been considerable objection to the employment of drying oils or the substances containing them on the grounds of insufficient durability. This objection is somewhat unreasonable, especially as a really cheap and adequate substitute has yet to be discovered. Probably a complete study of the drying process would go far to remove the complaint. It may be

[11] *Ber.*, 1916, **49**, 722; *J.*, 1916, 608.
[12] *Cf.*, however, the behaviour of methyl-α-elæostearate on distillation.
[13] *Ber.*, 1916, **49**, 1194; *J.*, 1916, 745.
[14] *Drugs, Oils, and Paints*, 1914, **30**, 207.
[15] P. H. Walker, *Proc. Am. Soc. Testing Materials*, 1915, **15**, I, 186.
[16] *Farbenzeit.*, 1915, **20**, 53, 877.
[17] *Ibid.*, 1914, **20**, 159.
[18] *Kunststoffe*, 1915, **5**, 4950.

mentioned here that varnishes for balloon covers made from boiled linseed oil are considered to be gastight.[19]

During the period under review no contributions to the solution of the problems of blooming have been published. The statements appearing in textbooks still remain, and each maker of varnish has his own views as to the cause and methods of prevention. There is one aspect of the subject which does not appear to have been considered—viz., the possibility of isomeric change in the oil during the process of drying and hardening of the varnish layer. It will be admitted that, apart from the mapping and cracking of many types of wood oil varnishes, there is a bloom which most probably is due to isomeric change in the glyceride whereby a white, crystalline, solid body is formed of which the oxidation product is likewise solid.[20] The presence of unoxidized oil in the varnish layer will favour the production of a small quantity of white substance, causing a cloudiness and loss of lustre. A similar isomeric change may occur in certain linseed oil varnishes under special conditions and be the cause of the loss of lustre. Such a view may appear inadequate to explain many of the cases of blooming, but experience of the behaviour of many varnishes gives considerable support, and the hypothesis is in agreement with some of the methods employed to prevent the occurrence of the defect.

Properties of Pigments.

W. Ostwald[21] discusses the foundation of a theory of pigments and classifies them according to colour, covering power, and effectiveness or strength. Colour is determined by the selective absorption of the pigment, and includes three factors : colour tone, or the location of colour on a circle consisting of prismatic colours, with the red and blue ends united by passing through purple ; brightness, or the fraction of light reflected as compared with amount reflected from pure white under the same conditions ; purity, a given colour is a mixture of a pure colour with grey, and the percentage of pure colour is the purity. Covering power is measured by the number of square cms. of surface which can be covered by one gram of pigment, so that the covered surface will not show through. Effectiveness of colour is defined by the ratio in which the colour and white pigment may be mixed before the colour disappears. With decreasing size of particles the covering power increases to a maximum and diminishes again when the size of the particles approaches the

[19] *Chem. Rev. Fett Harz Indust.*, 1915, 22, 27.
[20] Morrell, *J. Chem. Soc.*, 1912, **101**, 2082.
[21] *Koll. Zeits.*, 1915, **16**, 1.

wave-length of visible light waves. The effectiveness of colour varies with the size of the particles, and appears to be greatest when the degree of fineness is that corresponding to molecular dispersity. The strength is also determined by the magnitude of the coefficient of light absorption.

The light reflecting values of paints is the subject of a paper by H. A. Gardner,[22] wherein it is shown how the amount of light reflected from any given surface is measured and expressed in terms of the amount of light falling upon that surface, and to what extent different pigments affect the temperature of objects upon which they are laid. A scientific expression of the influence of pigments on the general comfort of any decorative scheme of colour is of very considerable interest. The reflection from painted surfaces is discussed by L. Bell,[23] who points out that oil paints have higher coefficients than water paints, those with traces of yellow giving the best reflection, and among colours fatal to good reflection are traces of black, red, blue, and deep yellow.

The vapours emitted by paint films have been examined by H. A. Gardner[24] and W. H. King ;[25] the latter criticizes Gardner's conclusions as to the production of carbon monoxide except in traces. King considers that the whole problem of the drying of linseed oil, alone or as an oil paint medium, is one of extreme difficulty. The theories are unsatisfactory, and a wide field of scientific investigation is open. One result of Gardner's researches is of special interest, viz., oil paints containing lead or zinc pigments do not evolve volatile compounds of a metallic nature, although aldehydic substances are present of which the effect will be bactericidal. Gardner's results have also been criticized by C. A. Klein.[26] The British Departmental Report,[27] recommending the prohibition of any paint material containing more than 5 % of its dry weight of soluble lead, has been considered by one authority to sound the death knell of the British white lead industry. The amount of soluble lead is to be determined by treating the dry matter, free from water, varnish, etc., with 1,000 times its weight of dilute hydrochloric acid (0·25 % HCl) and estimating the dissolved lead. The minority report urges the trial of the regulations before prohibition of lead paints.

The lessons from the 1906 Test Fence of the North Dakota Experimental Station[28] are of the greatest practical interest. The most

[22] *J. Franklin Institute*, 1916, **181**, 99; *J.*, 1916, 263.
[23] *Elec. World*, 1915, **65**, 211.
[24] *J. Ind. Eng. Chem.*, 1914, **6**, 91 ; *J.*, 1914, 266.
[25] *Ibid.*, 1915, **7**, 502.
[26] *Ibid.*, 1915, **7**, 99.
[27] *J.*, 1915, 561.
[28] E. F. Ladd and W. Washburn, *Bulletin*, 1915, **1**, 73.

important conclusions drawn are as follows:—Substitution of benzine for turpentine does not not give the same results as where turpentine in moderate amount is used. Sublimed white lead is not inferior in durability to basic lead carbonate, but sublimed white lead chalks more than basic lead carbonate. It is estimated that a three years' fence trial corresponds to a five years' house trial, but the character of the timber influences the lasting qualities of the pigment. According to G. W. Thompson[29] there is no evidence of any material chemical action ensuing between white lead and linseed oil, although a small amount of lead is dissolved, giving toughness and elasticity to the film.

E. W. Boughton[30] confirms this result, and points out that if the linseed fatty acids are in contact with white lead or zinc white, the zinc combines with four times as much acid as in the case of lead. White lead has the greater accelerating action on the oxidation of raw linseed oil. Raw linseed oil with chrome or zinc yellow undergoes no change out of contact with the air.

H. A. Gardner[31] considers that many of the defects of painting may be prevented by using paints of a composite class based upon white lead pigments, containing sufficient zinc oxide (25–50 %) to present a fine hard film. Previous treatment of wood with zinc chloride is recommended. When paste pigments are thinned by the painter, good clarified oil should be used. The use of linseed oil containing "foots" and moisture is stated to be responsible, wholly or partially, for "washing" and "brown spotting" of painted wood.

The importance of the composite pigments (lead and zinc) is referred to in the Report of American Society for Testing Materials.[32] Painting defects, and their prevention, are further dealt with by G. W. Thompson.[33]

The permanence of colour pigments has been studied by W. de W. Abney,[34] who showed that the use of a slow current of ozone in a few hours gave nearly the same results as those obtained by months of exposure to ordinary daylight, but moisture, not hydrogen peroxide, must be present. The darkening of lithopone is considered by W. J. O'Brien[35] to be caused by the production of zinc by the action of light on zinc sulphide, and all the patented processes for its prevention depend on

[29] *Drugs, Oils, and Paints*, 1915, **30**, 375.
[30] *U.S. Bureau Standards*, Tech. Paper **71**, 1916; *J.*, 1916, 852.
[31] *J. Franklin Inst.*, 1915, **179**, 681; *J.*, 1915, 805.
[32] P. H. Walker, *Proc. Am. Soc. Testing Materials*, 1915, **15**, Part I, 186.
[33] *J. Ind. Eng. Chem.*, 1915, **7**, 136.
[34] *J. Roy. Soc. Arts*, **63**, 85–91; *J.*, 1915, 39.
[35] *J. Phys. Chem.*, 1915, **19**, 113; *J.*, 1915, 290.

the formation of an insoluble film around the zinc sulphide, which prevents its reduction. R. B. Llopart[36] has patented a form of stable lithopone, and his claim is based on calcination of the zinc sulphide at 700° C.

L. Bock[37] concludes that the grouping of Na, Al, and SiO_2 in the ultramarine molecule is similar to that in zeolites, because of its formation from them by treatment with alkali sulphides.[38] The state of combination of sulphur in the various products is still doubtful. He concludes that ultramarines rich in silica approximate to double silicates, those rich in alumina to aluminium silicates, and sodium is less readily replaced in the double silicates than in aluminium silicates. The existence of isomeric ultramarines containing $-SNa$ or $-SONa$ groups attached to Al or Si respectively is considered probable. The relationships between blue, green, purple, and red ultramarines is discussed, and it is pointed out that a higher burning temperature can be used with mixtures rich in alumina than with those rich in silica.

The same author has investigated iron cyanogen colours.[39] He considers that the distinction between Paris and Prussian blues is founded upon the purity of the colour, which depends upon the quality of the substances used in manufacture. The presence of $FeFe(CN)_5CO$ imparts a violet tinge to the finished blue. The large variety of shades of Prussian blue are due to conditions of temperature and concentration of the solutions, and to the method and extent of the oxidation. The chief difference of steel and Milori blues from Paris and Prussian blues is probably of a physical nature, and is not due to higher content of potassium and less iron.

With the object of explaining the formation and nature of variously tinted forms of chrome yellow, Milbauer and Kohn[40] have investigated the system,

$$PbSO_4 + K_2CrO_4 \rightleftarrows PbCrO_4 + K_2SO_4$$

from the point of view of the phase rule and chemical equilibrium. The reaction proceeds almost completely from left to right, and at such a rate that it can be readily followed. The reverse action is very slight. The existence of lead sulphochromates is unlikely from the results of the authors' experiments. The determination of the mass action curve was very difficult owing to the very small equilibrium constant and the strong adsorption, which is of importance in the manufacture of

[36] Eng. Pat. 100092/1916; U.S. Pat. 1139437; *J.*, 1915, 670.
[37] *Z. angew. Chem.*, 1915, **28**, 147–52; *J.*, 1915, 561.
[38] *J.*, 1910, 577. [39] *Z. angew. Chem.*, 1916, **29**, 166; *J.*, 1916, 610.
[40] *Z. Physik. Chem.*, 1916, **91**, 410; *J.*, 1916, 972.

particular shades of chrome yellow. As a general result, chrome yellows may be made from lead sulphate, and the various shades can be obtained by varying the conditions, temperature, concentration, and time. An excess of lead acetate should be used so as to ensure absence of potassium chromate from the product, which would rapidly convert the lead sulphate (necessary for any particular shade) into lead chromate.

M. Toch[41] is of the opinion that spar varnishes and varnishes made with thickened linseed oil, or with open kettle boiled oil, are the best paint vehicles as protective agents against corrosion.

H. A. Gardner[42] confirms Toch's views, and recommends that a protective coating of paint for iron in cement and concrete structures should contain a vehicle of boiled oil or an oil drying by polymerization with a coarse pigment of the basic or chromate type to induce passivity of the metal. Ahrens[43] prefers heated China wood oil as a vehicle. Reference must be made to the report on testing of paint vehicles[44] (China wood oils) issued by the American Society for Testing Materials, one of the excellent series issued by the Society.

One of the most important contributions to the scientific study of pigments and paints is from H. A. Gardner,[45] who has investigated the conditions of opacity or hiding power of a pigment. The hiding power is greater the greater the degree of fineness up to a certain limit, the higher the refractive index, and the smaller the amount of oil absorbed by the pigment, which latter condition is of great practical importance. Several additional facts of considerable interest appear in the paper. A microscopical examination of lithopone indicates that the particles of barium sulphate are coated with zinc sulphide, mixtures containing barium sulphate and zinc sulphide possessing inferior covering power. The adhesive properties and cementing values of paint pigments increase with approach to the colloidal condition, the pigment forming a colloidal suspension in the oil.

The foots in linseed oil and in varnish appear to be present in the form of a colloidal suspension, and for their removal centrifuging is recommended.[46]

Natural Resins, Colophony, and Ester Gums.

The most interesting scientific work of the period under review is the synthesis of hydrourushiol dimethyl ether by M. Majima and T. Tahara.[47] The dimethyl ether was proved to be identical with that

[41] *J.*, 1915, **34**, 592. [42] *J. Ind. Eng. Chem.*, 1915, **7**, 504.
[43] *Drugs, Oils, and Paints*, 1915, **30**, 327. [44] *Ibid.*, 1914, **30**, 138 and 211.
[45] *J. Ind. Eng. Chem.*, 1916, **8**, 794; *J.*, 1916, 1025.
[46] Ayres, *J.*, 1916, 676. [47] *Ber.*, 1915, **48**, 1593 and 1606; *J.*, 1916, 128.

prepared from the natural urushiol (the chief constituent of Japan lac), whereby its constitution was fixed, with the exception of the position of the double bonds in the side chain. Hydrourushiol dimethyl ether was synthesized from sodium dodecine and 2.3-dimethylphenylpropionyl chloride and subsequent reduction.

$$\begin{aligned} &NaC{\equiv}C(CH_2)_9CH_3 + (CH_3O)_2C_6H_3(CH_2)_2COCl \\ &= (CH_3O)_2C_6H_3(CH_2)_2CO{\cdot}C{\equiv}C(CH_2)_9CH_3 + NaCl \\ &\qquad\qquad\downarrow \\ &(CH_3O)_2C_6H_3(CH_2)_2CO{\cdot}CH_2{\cdot}CH_2(CH_2)_9CH_3 \longrightarrow \\ &(CH_3O)_2C_6H_3(CH_2)_2CH_2CH_2CH_2(CH_2)_9CH_3 \end{aligned}$$

3.4-Dihydroxy-l-pentadecylbenzene (isohydrourushiol) was prepared and a new synthesis of isohydrourushiol dimethyl ether was effected whereby a comparison of the two dimethyl ethers could be made.

Two groups of resins, Euphorbia and Elemi (from Mauritius),[48] are of no present value for varnish making. Pontianak (Jelutong) rubber resin is similar to the above, and is remarkable for its resistance to alkalis. The resin contains 10 % rubber, 20 % resin, and 70 % moisture.[49] The resins of *Picea vulgaris* (Transylvanian pine) and Jura turpentine are not identical according to H. Binder.[50] The examination of the resin by Tschirch's method showed that four picea-pimaric acids could be isolated. M. Henze[51] considers that the solid constituent of Storax balsam (*Liquidambar orientalis*) is not a single storesinol, $C_{16}H_{26}O_2$, in combination with cinnamic acid as stated by Tschirch and van Itallie, but that it is a mixture of five or six distinct substances. The major part of the resin consists of a mixture of two isomeric acids, $C_{20}H_{30}O_2$, identical with abietic and pimaric acids. This is the first instance of the occurrence of these acids in resin from a non-coniferous tree. A. Tschirch and C. der Jong[52] have continued their investigations on the composition of resins, and have published a communication on amber (succinite). Aweng's succinoabietic acid has furnished two acids, succino-oxyabietic acid, $C_{19}H_{29}O_2COOH$, and succino-abietinolic acid, $C_{39}H_{59}O_3COOH$. The main constituent of amber is succinoresene, which is the cause of its resistance to the action of reagents.

According to U.S. Commerce Report, No. 281, 1915, it is estimated that 350,000 tons of kauri gum is still available in New Zealand, or a 40 years' supply at the present rate of output. The export trade

[48] *Bull. Imp. Inst.*, 1915, **13**, 357; *J.*, 1915, 1216.
[49] Dubosc, *Caoutchouc et Guttapercha*, 1915, **8**, 5756.
[50] *Arch. Pharm.*, 1914, **252**, 547–589; *J.*, 1915, 805.
[51] *Ber.*, 1916, **49**, 1622; *J.*, 1916, 1025.
[52] *Arch. Pharm.*, 1915, **253**, 290; *J.*, 1916, 129.

from the Crown Lands (approximately half of the known kauri gum field) is now controlled by the Minister of Lands.

The extraction of resin from wood by petroleum solvents has been shown by R. C. Palmer and H. R. Boehmer[53] to be complete and the spent wood chips can be used for paper pulp or for fuel. L. Paul[54] describes combinations of abietic acid with benzine and higher boiling petroleum hydrocarbons and shows that the property is extended to its salts—*e.g.*, sodium pinate gives a solution with ten times its weight of petroleum, and the solution solidifies to a colourless translucent mass. Such combinations are of considerable interest from a practical point of view. Paul also states that American colophony contains 90% pinic acid (m.pt. 70° C.) together with sylvic acid, m.pt. 122° C. The two acids are transformed on standing into α-pinic (m.pt. 100° C.) and β-pinic (m.pt. 122° C.) acids; moreover, when α- and β-pinic acids are recrystallized from alcohol, α-, β-, and γ- abietic acids are obtained. The basis of autoxidation of colophony is α-pinic acid, which undergoes conversion into β-pinic acid. The resenes of colophony are of low oxygen content and may be regarded as oxypolyterpenes formed from terpenes by simultaneous polymerization and oxidation.

Abietic acid from Spanish colophony is identical with the acid obtained from American colophony.[55] L. G. Radcliffe and C. W. Palmer[56] have examined the metallic content of some linoleates and rosinates, and give a description of the different salts and some of the uses for which they have been suggested.

The properties of ester gums have been investigated by Ellis and Rabinovitz,[57] with special consideration of prevention of "livering" of the vehicle in the presence of pigments. Rosieki[58] considers that the reduction in the acidity of gums is a necessary factor, whereas Muehle[59] is of the opinion that coagulation is due to association of copal particles rather than the formation of insoluble salts, because he was unable to produce varnishes from Congo and Manila copals, which stand the addition of pigments either after esterification or reduction in the acid value. Meguele[60] considers that there is truth in both views, and the verdict of practical experience with copal varnishes will support Meguele.

[53] *J. Ind. Eng. Chem.*, 1916, **8**, 695; *J.*, 1916, 972.

[54] *Z. angew. Chem.*, 1915, **28**, Ref., 415 and 337; *Seifensieder Zeitung*, 1915, **42**, 640, 659; *J.*, 1916, 1062, 1153.

[55] Blanes, *J. Chem. Soc.*, 1915, **108**, 1493; *J.*, 1915, 878.

[56] *J.*, 1915, 644.

[57] *J. Ind. Eng. Chem.*, 1916, **8**, 406; *J.*, 1916, 698.

[58] *Farben-Zeitung*, 1913, 1194.

[59] *Ibid.*, 1913, **119**, 1944, 2058, 2178.

[60] *Ibid.*, 1913, 2230.

Ellis' paper is of interest as giving a valuable summary of the published work to date, although it does not present a solution of the difficulty. The resistance of ester gums to the action of alkaline solutions is a most important property as affecting the durability of varnishes, and the subject is deserving of active experimental work. H. Terrisse and the Indestructible Paint Co.[61] describe the formation of glycerin ester gums prepared from copals, rendered soluble by their patented method[62] or by the usual method, alone or mixed with copal oil. It is claimed that such varnishes can be ground with an equal weight of zinc white to form a paint.

Synthetic Resins.

The many varieties of combination of phenol and its homologues with formaldehyde and its derivatives form the basis of numerous patents and the subject of patent cases.[63]

G. Matsumato[64] has investigated the conditions of the formation of phenol and formaldehyde, with special reference to Bakelite, including crystallizable, soluble, and fusible varieties. The process proceeds in three stages—initial condensation, concentration of products, and hardening. As condensing agents, acids, alkalis, hexamethylenetetramine, phenylhydrazine, and sodium sulphite have been used, but neutral salts have no effect. Caustic soda is the best condensing agent and ammonia the most successful hardener; in fact, only basic substances are employed as hardeners. Cresol and formaldehyde give analogous products to Bakelite. Lemme's method of estimating formaldehyde was used with satisfactory results.

Attempts have been made to employ such synthetic resins in oil varnishes and they form the basis of patents by K. Albert and L. Behrend.[65] It would appear that the assistance of colophony, cumarone resin, or a natural resin was necessary to bring about solution in linseed oil.

Phenol-formaldehyde products may be combined with casein (acting as a condensing agent similar to alkalis). The resinous products are considered by H. Kuhl[66] to have a wide technical application, and his

[61] Eng. Pats. 23054 and 23055/1914, *J.*, 1916, 57.

[62] *J.*, 1904, 582; 1908, 457.

[63] F. Pollak, Eng. Pat. 20977/1914; A. Heinemann, H. C. Harvey, and H. W. Robinson, Eng. Pat. 28187/1913; A. Heinemann, Eng. Pat. 9390/1914; S. Karpen & Bros., Eng. Pat. 9292/1914; K. Tarassof, Fr. Pat. 470810 (1914); *J.*, 1915, 187, 623, 879, 1154.

[64] *J. Chem. Ind. Tokyo*, 1915, **18**, 434; *J.*, 1915, 1104.

[65] Eng. Pat. 15875/1914 and Ger. Pat. 281939 (1913); *J.*, 1915, 724, 805.

[66] *Chem. Ind.*, 1914, **37**, 559; *J.*, 1915, 561.

comparison of the casein-cresol spirit lacquers with Bakelite is favourable.[67] Viscose,[68] and even glue,[69] in the presence of glycerin may be combined with aldehydes and phenol or an amine to give hard or plastic substances. The polymerization products of vinyl esters (vinyl acetate or vinyl chloracetate) by ultra-violet light yields solid masses which may serve as substitutes for celluloid and which are fire-proof and odourless. The polymerization is assisted by catalytic agents (organic peroxides) to give thick syrups which on illumination give valuable solid masses.[70]

F. E. Matthews and H. M. Elder[71] claim that compounds of sulphur dioxide and unsaturated hydrocarbons (pseudobutylene, propylene, amylene, and ethylene) are polymerized after exposure to ultra-violet light or by heating. The butylene body gives a transparent film and renders celluloid less inflammable. A review of synthetic resins is given by R. Eller,[72] with special reference to the patent literature.

F. Steinitzer[73] has investigated the methods of detecting the constituents of phenol-formaldehyde resins. The phenols can be liberated by soda-lime ; if starch is present it can be detected by tests applicable to dextrin. If casein is a component the sulphur therein must be removed by lead oxide before the tests for phenols are tried.

A new class of artificial resins (cumarone resins) has attracted some attention during the war, especially in Germany. These resins are the polymerization products of cumene and indene (obtained from crude benzene by the action of sulphuric acid). They are the subject of a number of patents[74] and a review and discussion of the patented processes has been given by M. Bottler.[75] C. Ellis and L. Rabinovitz,[76] by treating solvent naphtha (b.pt. 160°–180° C.) with 1 % sulphuric acid (sp. gr. 1·84), obtained a transparent resin-like residue of the consistency of molasses which could not be hardened by polymerizing agents. On distillation in a vacuum, 50 % of a solid resin was left which gave films from benzol solution and resisted alkaline aqueous extracts of cement.

[67] *Kunststoffe*, 1915, **5**, 196.
[68] J. M. Taylor, U.S. Pat. 1172073 (1916), *J.*, 1916, 429.
[69] Usher Walker and C. Sohn, Eng. Pat. 2167/1915 ; *J.*, 1916, 368.
[70] Ger. Pats. 281687 and 281688, *J.*, 1915, 623.
[71] Eng. Pat. 11635, 1914, *J.*, 1915, 670.
[72] *Kunststoffe*, 1916, **6**, 45.
[73] *Ibid.*, 1915, **5**, 109 ; *J.*, 1915, 1153.
[74] M. Wendriner, Ger. Pat. 281432 (1913) ; R. Lender, Ger. Pat. 277605 (1913) ; A. Eichler, U.S. Pats. 1133432 and 1133438 (1915) ; *J.*, 1915, 187, 561, 623.
[75] *Kunststoffe*, 1915, **5**, 277.
[76] *J. Ind. Eng. Chem.*, 1916, **8**, 797 ; *J.*, 1916, 1025.

Cellulose Varnishes.

The acetates of cellulose and their solvents for the production of varnish coatings are the subject of a number of patents which have been reviewed by L. Clement and C. Riviere.[77] The favourite solvent was tetrachloroethane or other chlorine derivative of an aliphatic hydrocarbon, but it has been found necessary to restrict its use[78] and substitutes have been employed. Cellon varnish[79] is stated to consist of acetylhydrocellulose and a neutral softening material. It is proof against oils, fats, acids, and alkalis and is used as a non-corrosive paint, being as hard as rubber and not so brittle, and having very high insulating powers.

Much work is being done in connection with cellulose coatings and a careful study of their durability is very essential. The importance of the composition and properties of such materials is of the highest in aeronautic work. It is to be hoped that after the war the progress made in this direction will be published.

Turpentine.

From a practical standpoint the progress in connection with turpentine is very limited. In the Year-book of the American Society for Testing Materials[80] details for a standard specification of American turpentine are given which are of considerable value to consumers.

A. W. Schorger[81] has shown that the phyto-chemical processes occurring in the leaves and in the woody portions of certain *Coniferæ* are different, the oil from the former consisting of aromatic compounds, chiefly terpenes in the case of *Pinus Sabiniana* (digger pine), whilst from the latter aliphatic derivatives are obtained. The oleoresins of the above pine give an oil consisting almost entirely of normal heptane. According to M. Adams[82] redistilled Jeffrey pine wood turpentine gave 90 % of normal heptane. As a result of the examination of single leaf nut pine, Jeffrey pine, and Western yellow pine, it was found that the turpentine oil from the wood and oleoresin are similar in character.

Methods of Testing Varnishes and Varnish Analyses.

The unreliability of methods of varnish analyses is very marked and the absence of standard methods is much to be regretted. Some

[77] *Bull. Soc. D'Encouragement*, 1914, **121**, 187; *J.*, 1915, 75.

[78] J. H. Hardcastle and A. H. Taylor, Eng. Pat. 13100/1914, *J.*, 1915, 146; W. H. Willcox, *Lancet*, 1915, **188**, 544; *J.*, 1915, 508.

[79] *Elektrotechn. Z.*, 1916, **37**, 109.

[80] *American Society for Testing Materials*, 1915, 428.

[81] *J. Ind. Eng. Chem.*, 1915, **7**, 24; *J.*, 1915, 197.

[82] *Ibid.*, 1915, **7**, 957; *J.*, 1915, 1215.

investigators conclude that chemical analyses are of no value in testing varnishes except for determination of the amounts of thinners and for the detection of colophony, but this view is undoubtedly too pessimistic. The difficulty of separation of polymerized oil from unthickened linseed oil in a varnish might be overcome by using the acetone method.[83] R. W. Darner[84] describes a method which is said to be very accurate, depending on the removal of the hard gums by precipitation with light petroleum (0·670) and separation of colophony from the oil by Twitchell's method. The presence of polymerized China wood oil causes a deposit of the oil with the copals, but the precipitate does not adhere to the sides of the flask as in the case of the copals. Stress is laid on the quality of the petrol used. E. W. Boughton[85] points out that the precipitation with light petroleum does not separate the gum quantitatively and he describes a method of estimation of resin and oil in varnishes based on the removal of the unsaponifiable matter by alkali in the presence of benzol, esterifying by Wolff's method, separation of the resin acids, and estimation of the fatty acids in the usual manner. It was found that 7 % of the total resin was weighed with the fatty acids. The author concludes that the results are fairly accurate.

In another communication the author describes the methods for the detection of colophony in driers. By the application of Wolff's esterification method, colophony above 6 % of the ash-free non-volatile portion of the drier can be detected.

M. Seaton and G. B. Sawyer[86] have published the first of a series of papers on varnish analyses and varnish control entitled "Molecular Weights of Vegetable Oils." By using stearic acid as solvent, values for the molecular weights of oils were obtained which varied only slightly with the concentration of the solution. The acids obtained from the oils gave corresponding values for molecular weights by the cryoscopic method, using stearic acid as solvent. The process is simple and it is satisfactory to have a solvent which can be used for oil and acid alike.

An excellent summary of standard methods for testing varnishes is given in *Drugs, Oils and Paints*.[87] It is of considerable practical value, especially in reference to the examination of plate and paper films of varnish. Chemical analyses are considered of little value except for the estimation of thinners and for the detection of colophony.

[83] Morrell, *J.*, 1915, 105.
[84] *N. Dakota Agric. Expt. Sta., Paint Bulletin*, 1915, **1**, 108.
[85] *U.S. Bureau Standards*, Techn. Paper, 1916, 65.
[86] *J. Ind. Eng. Chem.*, 1916, **8**, 490; *J.*, 1916, 746.
[87] *Drugs, Oils, and Paints*, 1915, **31**, 249; 1916, **32**, 326.

J. F. Sacher[88] has described a colorimetric method for the detection of manganese in pigments and varnishes which seems to be quite reliable and delicate. A small quantity of the material is incinerated, the ash dissolved in dilute acid, filtered, and the solution made slightly alkaline; on addition of a 3 % oxalic acid solution to dissolve the manganese hydroxide a red coloration is produced when as small a quantity as 0·05 mgrm. manganese is present in 0·1 grm. of the substance. The test is reliable, even in the presence of a cobalt salt. The coloration is due to the formation of a double salt, possibly $K_3Mn(C_2O_4)_3 3H_2O$.

G. W. Knight and C. T. Lincoln[89] recommend a method of estimation of methyl and ethyl alcohols in spirit varnishes based on the transformation of the alcohols into iodides, or if the percentage of methyl alcohol is less than 10 %, the alkyl iodides can be estimated by a method based on Riche and Bardy's qualitative test (*Comptes rend.*, 1875, **80**, 1076). The results are stated to be satisfactory, but the details of the method are elaborate, and it is not rapid.

J. A. Schaeffer[90] describes a rapid method of analysis of red lead and orange mineral depending on the estimation of lead peroxide produced on treatment with nitric acid and subsequent addition of a known quantity of hydrogen peroxide. The excess of hydrogen peroxide is estimated by permanganate. A blank test is made with the same volumes of hydrogen peroxide and nitric acid.

The effects of storage of mixed paints containing an aqueous emulsifying agent are described by E. Ware and R. Christman.[91] To prevent the formation of an amorphous soapy layer on the settled pigment it is suggested that an aqueous emulsifying agent, containing a substance which does not saponify linseed oil, should be used, or a non-aqueous protective colloid, such as aluminium oleate or palmitate, to prevent settling of the pigment. The setting of mixed paints might be prevented by grinding the pigments in an oil of fairly high acid content, or by adding the optimum amount of lead or zinc soap to the pigments ground in a neutral oil.

G. Cohn[92] has described a series of resin acids, produced by condensation of formaldehyde and phenoxyacetic acid, which are characteristic of a whole group of compounds. They can also be prepared by condensing alkali-soluble phenol-formaldehyde resins with chloroacetic acid. The alkali salts of the resin acids, when added to

[88] *Farbenzeit.*, 1915, **20**, 1309; *J.*, 1916, 972.
[89] *J. Ind. Eng. Chem.*, 1915, **7**, 837; *J.*, 1915, 1103.
[90] *Ibid.*, 1916, **8**, 237; *J.*, 1916, 478.
[91] *Ibid.*, 1916, **8**, 879; *J.*, 1916, 1122.
[92] *Chem.-Zeit.*, 1916, **40**, 725; *J.*, 1916, 1025.

solutions of basic dyestuffs, give on treatment with acetic acid precipitates of the resin acids together with the basic dye. Tricresoxyacetic, resorcinoloxyacetic, and guaiacoloxyacetic resin acids are also described.

In consequence of the results obtained with artificial resins as regards their behaviour towards basic dyestuffs, Cohn[93] has extended his investigations to colophony. Colophony in dilute ammonia behaves in precisely the same manner as the artificial ammonium resinates, precipitating basic dyestuffs on addition of acetic acid. The pale green copper abietate, soluble in ether and almost completely insoluble in methyl alcohol, can be easily separated from small quantities of a copper salt of a resin acid present in varying amounts in colophony.

Remarkable gel formations were observed when colophony was treated with dilute aqueous ammonia. A pure form of abietic acid (m.pt. 156°–162° C.) can be obtained when colophony is treated with methyl alcohol and a little concentrated sulphuric acid and the separated abietic acid (28 % yield) recrystallized from methyl alcohol. In an attempt to ascertain the composition of colophony, pure abietic acid, heated to 160°–170° C. without losing weight, was found to possess the properties of the natural product. Cohn considers that the natural resin is not an anhydride of abietic acid, but a more or less impure acid in a vitreous form.

[93] *Chem. Zeit.*, 1916, **40**, 791; *J.*, 1916, 1070.

INDIARUBBER, Etc.

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This being the first of the Reports issued by the Society, it has been found necessary to refer back to processes and investigations antedating the period covered by this Report in order that the more recently published work may be understood. This has necessitated the exclusion of some matter for which otherwise room would have been found.

Statistics.

According to S. Figgis and Co.,[1] the production of indiarubber for the years 1914 and 1915 may be summarized as follows :—

	1914.	1915.
India and Ceylon	14,800 tons.	20,600 tons.
Malaya, Sumatra, Java, etc. ...	49,700 „	72,800 „
Brazil, Bolivia, Peru, etc.	37,000 „	37,500 „

Sources other than these, including Africa, contributed only some 15,000 tons in 1915. From these figures we may estimate that, out of a world's production of 146,000 tons, almost exactly two-thirds consisted of plantation rubber grown in the East. The output from South America hardly varies, but the tendency during the last few years has been to decline rather than to increase. It is obvious, however, that the huge increase in the output of plantation rubber, with the lower prices of the commodity, has not brought about the rapid diminution in supplies from the Amazon districts which was anticipated by some. It must not be forgotten that the actual proportion of plantation rubber produced is larger than these figures would indicate, as this rubber is mostly marketed clean and dry, while the best and cleanest South American brand—viz., fine hard Para—loses at least 20 % on washing and drying, and inferior brands much more. It would therefore appear that in 1915 the plantations furnished more nearly three-quarters than two-thirds of the world's output of rubber, if taken in the washed and dried state, ready for manufacture. The product of

the plantations is almost entirely rubber from *Hevea*. This also applies to the greater part of the output from Brazil. Consequently the rubber now being used by manufacturers consists almost entirely of rubber from *Hevea*, and rubber from other botanical sources tends gradually to disappear. Brazil was previously the sole source of *Hevea* rubber, and as *Hevea* yields the raw rubber of the highest class, the material now handled by the manufacturer has immensely improved since the introduction of plantation rubber.

The output of plantation rubber for 1916 is estimated at 140,000 tons —that is to say, an increase in yield over 1915 almost as great as the total yield of "wild" rubber.

Of plantation rubber it is estimated that 83 % is produced in British colonies and 90 % by British-owned companies.

Of the total production of raw rubber the United States imported 50 % in 1914 and 65 % in 1915.

Production of Raw Rubber.

Various methods of coagulation and treatment of rubber latex have been patented or described. The inventors in many cases do not specify the particular latex to which their process applies, but appear to take it for granted that what applies to plantation—*i.e.*, *Hevea*—latex, also applies to latices of other botanical derivation. *Hevea* latex, however, is more easily coagulated than any other of commercial importance. A trace of almost any acid or acid-reacting substance is all that is required, so that the "inventor" has a wide field for his activities. Thus acetic acid, sulphuric acid, alum, and other salts may be employed. The Dunlop Rubber Company[2] have patented the use of solutions of bismuth or zinc chloride. S. C. Davidson[3] treats latex with a solution of sodium thiosulphate in "alkalized cresol" (cresylic acids treated with caustic alkali), and subsequently coagulates with sulphuric acid. In previous patents formalin and liver of sulphur formed part of the solution added. As far as can be seen, there is no theoretical basis for such treatment nor any practical advantage to be gained. On the other hand, there is some danger of damaging the rubber from residues of chemicals added to the latex. Thus B. J. Eaton,[4] as a result of experiments in the treatment of rubber coagulum with caustic soda, sodium carbonate, or lime, states that "it is possible that a rubber of this type may be of considerable value commercially, in view of the remarkably rapid rate at which it vulcanizes." In a circular issued by the Rubber Growers' Association,[5] Beadle and Stevens show that rubber so prepared deteriorates on keeping, and sooner or later perishes.

Martin has also demonstrated the deleterious effect of alkaline substances on vulcanized rubber.[6]

B. J. Eaton and J. Grantham publish some results[7] obtained by allowing latex to coagulate spontaneously under conditions intended to prevent or modify the putrefactive changes which otherwise take place: It is well known that latex left in an open vessel for twenty-four hours or more coagulates spontaneously, but more or less imperfectly. The surface becomes covered with a yellow slime of alkaline reaction, while the underneath parts are acid. By exclusion of air, the development of the micro-organisms giving rise to the yellow slime and the putrefactive odour is largely inhibited. This so-called "anaërobic" process is the basis of a patent applied for in the Federated Malay States. Eaton and Grantham, however, find that coagulation with the exclusion of air is frequently incomplete. From experiments where latex was sterilized by heating, they conclude that coagulation can be produced by non-putrefactive bacterial action. They therefore propose to allow latex to coagulate spontaneously in the presence of substances such as sugar, which inhibit putrefactive changes. The amount required is stated to be very small, as, for instance, 0·2 % of dextrose calculated on the latex. Coagulation was complete in eighteen hours, and the coagulum had a sweet odour.

The Rubber Growers' Association have issued a table of recommendations for the treatment of latex and curing of rubber which could with advantage be reproduced in its entirety did space allow. It is a planters' *vade mecum*, or condensed textbook, on the preparation of plantation rubber, based on the experience of the Association's scientific officers in the East. As regards experimental work in connection with coagulation, that carried out under the auspices of the Rubber Growers' Association, and also the vulcanization tests at the Imperial Institute, are not submitted for general circulation. Important papers by G. Stafford Whitby[8] and by Eaton and Grantham[9] have appeared in this Journal and in the Malay bulletins. Whitby's paper is primarily concerned with a comparison of the Brazilian and plantation methods of preparing rubber from latex. Previous to the advent of plantation *Hevea* it was generally recognized that *Hevea* rubber, as prepared in Brazil, was the best obtainable. Hence plantation prepared rubber has frequently been judged by comparison with the former. The best quality, or fine Para, is prepared by the evaporation of thin superimposed layers of latex on a long pole or paddle-shaped piece of wood in the smoke from a fire. Whitby prepared rubber in this manner on a rubber estate in Malaya from the latex both of young and old trees, a portion of the latex being set aside for coagulation with acetic acid and

smoke-drying of the coagulated sheet as in the ordinary preparation of plantation smoked sheet rubber. From vulcanization tests made, Whitby concludes that, so far from the Brazilian method giving a better rubber, the results indicate that the plantation method yields at least as good a rubber, and probably a better one. This conclusion is in accordance with other experience. H. P. Stevens,[10] however, points out that there is some doubt whether the Brazilian method of preparation was exactly adhered to, as the moisture in Whitby's sample was but little more than half that commonly present in fine hard Para. Nevertheless, it is now fairly certain that fine hard Para does not differ materially in quality from plantation *Hevea* rubbers. This disposes of the various conjectures put forward from time to time to "explain" the superiority of the Brazilian over the plantation product.[11]

It is now frequently asserted that, although specimens of plantation rubber may equal specimens of fine hard Para, or even surpass the latter, nevertheless fine hard Para is a superior product from the manufacturer's standpoint, because of its greater "uniformity." The term "uniformity" has been used in various senses, and the matter has been argued and discussed *ad nauseam*. Without entering on this discussion, it may be noted that Sidney Morgan[12] points out that, if the quality of the rubber varies from day to day, a loaf of fine Para will be composed of parts which are not really uniform, or, as Eaton[13] puts it, the method of preparation of fine hard Para results in the averaging of the latex collected daily over a long period. This would correspond to the averaging of say a number of smoked sheets taken from the daily output of an estate over a considerable period. Whitby[14] has carried the research a stage further by investigating the effect of phenols on *Hevea* latex, it being assumed that the phenolic substances in the smoke affect the properties of smoked rubber, and concludes that they retard the rate of cure. In fact, he comes to the conclusion that there is no evidence to show that smoking improves the quality of rubber, and quotes comparative tests on smoked and air dried sheet to show that in many cases the latter form is superior, while smoking of crepe rubber may cause serious deterioration. He also believes that "oxidation in itself has no ill effect on the quality of rubber." He appears, however, to refer to the oxidation of the latex or latex serum and not to the rubber. He speaks of the outer layers of a ball of fine Para as being "more oxidized" than the inner layers, and, as the result of vulcanization tests, concludes that there is no difference in quality between them. This is contrary to the generally accepted belief that the outer dried layers are inferior.

Stevens[10] points out that the conclusions reached by Whitby and

others are only of value provided that the tests are carried out on rubber correctly vulcanized. This can be shown by ageing tests, which were not made.

A number of patents have been taken out for exposing latex in thin films on plates or drums to a smoky atmosphere which has the effect of both coagulating and smoking the latex as in the case of native Brazilian rubber.[15] These all appear more cumbersome and expensive than the ordinary methods in vogue without possessing any corresponding advantages. Patents have also been taken out for processes of coagulation after concentration of the latex by evaporation.[16] This, however, would produce a skin of coagulated rubber on the surface so that the further treatment of smoking in thin films as suggested would appear impracticable. Evaporation must take place in many of the processes suggested for coagulation in thin films, the deposition of the rubber being only partly due to ordinary coagulation. Rubber obtained by evaporation of latex is, according to M. Kerbosch,[17] less readily oxidized under the influence of sunlight than that produced by coagulation. This result is attributed to certain unidentified soluble constituents presumably retained in the evaporated latex, but which would be lost in the serum after coagulation.

The Non-caoutchouc Constituents of Rubber Latex.

Some discussion has arisen in regard to the non-caoutchouc constituents, although nothing further has been done by way of isolation or identification. It will be remembered that D. Spence[18] was the first to recognize the nitrogenous nature of the "insoluble constituents" of raw rubber, and that further work was carried out by Beadle and Stevens.[19] The insolubility refers to organic solvents such as chloroform and benzene, in which the caoutchouc dissolves, although the high viscosity of the solution renders the separation of the insoluble constituent a very tedious operation. Spence[20] subsequently found that the viscosity of the solution could be rapidly reduced by the addition of a small quantity of trichloracetic acid, which brings about a rapid "depolymerization" of the rubber in solution. G. Bernstein[21] employs ultra-violet rays for the same purpose, a two-per-cent. solution of the rubber in petrol spirit being exposed to the light from a Westinghouse lamp with the exclusion of air. In three minutes the viscosity of the solution falls to a point at which it is hardly more viscous than the original solvent, so that separation can be effected by decantation or filtering. F. Frank[22] achieves the same end by heating the rubber in a test tube with boiling cymene, limonene, or dipentene until broken down. The solution is centrifuged. The clear liquid is poured off, fresh solvent added, and

the liquid again centrifuged. The process is repeated with benzene, and again with ether, and the residue dried. All these processes are open to the criticism that the heat or other disintegrating agent employed may have some action on the insoluble constituent.

It is well known that the non-caoutchouc constituents of latex exert a profound influence on the vulcanizing properties of rubber, and removal of the protein (insoluble constituent) causes the rubber to cure more slowly.[19] Eaton and Grantham find that the rate of cure depends on the amount of serum retained in the coagulated rubber.[23] They find that so-called slab rubber cures faster than sheet rubber, because in the former the coagulum is not rolled, and therefore retains more of the serum. They also find that sheet rubber cures faster than crepe rubber, and explain this in a similar manner, the thorough washing of crepe rubber removing the serum very effectively. They point out that the increased rate of cure may not be due to the protein or other constituents of the latex but to decomposition products formed subsequently from these constituents. Reference will be made later to the so-called "accelerators," organic nitrogenous derivatives which increase the rate of vulcanization. Eaton and Grantham refer to these, and suggest that similar substances may be formed by the decomposition of the proteins in the latex. These substances have not as yet, however, been isolated or identified. Eaton and Grantham also find that smoking retards the rate of cure, and that the addition of preservatives has a similar effect. If the increased rate of cure is caused not by the additional serum retained in the rubber, but by some catalyst produced therefrom by the agency of an enzyme, then smoking might have the effect of destroying the enzyme or other agency by which the accelerating substance is produced, restricting its formation, thus yielding a slow curing rubber. They also obtain a rapidly curing rubber showing good mechanical properties by allowing the coagulum to stand for a few days before further treatment. A period of six to ten days is sufficient to develop the maximum rate of vulcanization. The rubber may then be washed and creped without losing these properties. In another series of experiments,[24] the coagulum which had been allowed to stand for ten days was cut up into worm form and dried in a hot-air drier. This treatment resulted in a rapidly curing rubber of good mechanical properties in contrast with a control in which the coagulum was similarly treated without allowing it to stand before treatment. It is evident, therefore, that the catalyst or "accelerating" substance formed by allowing the coagulum to stand was not removed either by washing on the crepeing machine or heating in the drier.

F. Kaye[25] gives some figures for the percentage of phosphorus

contained in rubber latex. These confirm earlier figures of Beadle and Stevens, who gave figures for plantation latex varying from 0·06 % to 0·13 % P_2O_5 on the dry solids. Kaye's figures for fine hard Para are 0·05 to 0·08, and for good quality latex 0·05 to 0·12 %. On the assumption that the phosphorus is present as a nucleo-protein or decomposition product of the same, he is of opinion that the study of the quantity and nature of phosphorus in the latex would throw light on the changes taking place in the protein components. The suggestion is rather vague, and he supplies no additional data. When latex is coagulated, a part of the phosphorus is retained in the coagulum, and a part remains in the serum. It is probable that a part at least of the phosphorus is in intimate combination with the nitrogen, and may also form a constituent of the accelerating substance produced during putrefaction.

The Effect of Details in Preparation.

A series of experiments by Eaton has recently been published[26] to determine the effect of vacuum drying on crepe rubber as ordinarily prepared, that is to say, washing and crepeing the same day or the day after coagulation. From a number of experiments giving varying results, he concludes that the physical properties of vulcanized rubber undergo no deterioration by vacuum drying. The addition of sodium bisulphite to the latex previous to coagulation gave a product yielding similar results. The amount of sodium bisulphite used is not stated, but it evidently exercised no restraining effect on the formation of the accelerating substance. Sodium bisulphite was also without effect on the properties of crepe rubber as ordinarily prepared. It may be explained that the use of sodium bisulphite was introduced some years ago by the Rubber Growers' Association Chemists[27] for the purpose of preparing pale coloured crepe rubber, and the prevention of surface darkening, which takes place wherever the fresh coagulum is exposed to the air. A very small proportion—one part per 400 of latex or less—suffices to inhibit the action of the oxydase present in latex. Exhaustive experiments were made before the sodium bisulphite was recommended for this purpose. Its use became very general, and very little crepe rubber is now prepared without it. It was condemned by W. A. Williams[28] on what appears to be insufficient grounds. Nevertheless, the independent confirmation of its harmless nature by Eaton and Grantham is noteworthy. Previous to the introduction of sodium bisulphite, formalin had been used for a similar purpose, and also as an anticoagulant. Eaton and Grantham find that this antiseptic is without influence on the quality of thin crepe.

Eaton and Grantham have investigated the behaviour of crepe rubber from other standpoints. Thus they find that the number of times the rubber is put through the crepeing rolls is without appreciable influence on the mechanical properties and rate of cure.[29] Experiments were made with specimens passed as many as twenty-five times through the rolls. Only by severe maceration (not mere rolling) was a slight, although appreciable, retardation in rate of cure observed. The authors appear to conclude that nothing but excessive working affects the properties of the vulcanized rubber. This they attribute not to the mechanical effect of the working, but to the removal of traces of catalytic substance. In this connection it is interesting to note that Whitby[8] finds the crepeing of fine hard Para to be without effect on the properties, and Morgan[30] quotes figures to show that the crepeing of smoked sheet rubber is also without effect. Both Eaton and Grantham and Whitby agree, confirming previous work, that variation exists in the rubber prepared from the latex collected on different estates, or parts of estates, or even different groups of trees, and consequently all tests must be made with controls from the same latex. On the other hand, the normal output of crepe rubber from any given estate does not show appreciable variation. This, according to Eaton and Grantham, is caused by the fact that in the preparation of crepe all the serum containing the catalytic or other substance is washed out and the conditions of preparation do not vary. Whitby[8] finds a small improvement in the rubber when the latex is allowed to stand for a period previous to coagulation. This, taken in conjunction with Eaton and Grantham's results, appears to indicate that changes take place in the latex on standing similar to those which take place in the coagulated rubber.

Eaton and Grantham have also made experiments by varying the proportion of acid used for coagulation. Morgan quotes figures to show that an excess of acid is harmful, and Eaton and Grantham find that, by increasing the proportion of acid fivefold, the rubber produced cures a little more slowly.

J. Grantham[31] has published the results of a number of nitrogen determinations on different types of plantation rubber. The results are calculated to the third figure, which cannot possibly have any significance. The figures obtained for the smoked rubbers (sheet or slab) differ but little among themselves and are rather higher than for the unsmoked. The author concludes that smoking appears to fix the nitrogen. More variation is shown with the unsmoked rubbers, the slab form giving the lowest figures, especially after crepeing. The low figure for nitrogen is attributed to loss in the gaseous form during the

superficial drying of the slab, and partly to the washing out of nitrogenous decomposition products when the slab is creped. The association of a low nitrogen content with rapid vulcanization in air-dried rubber is interesting. As smoked slab rubber also vulcanizes rapidly, Grantham concludes that "the actual loss of nitrogen cannot be the cause of rapidity of vulcanization." Presumably it is intended to imply that the process by which the nitrogen is lost does not affect the efficiency of the catalyst or accelerating substance which remains.

Before leaving the subject of raw rubber preparation, a reference should be made to Whitby's tests on rubber from trees of different ages. The opinion has been widely held that rubber from young trees must necessarily be "less mature," and therefore inferior to that from old trees. It is certainly true that *Castilloa* rubber from young trees is inferior, for the reason that it contains a larger proportion of "resins" and a smaller proportion of caoutchouc. But in the case of *Hevea* rubber there is very little difference in the percentage composition of the raw rubber, although young trees may give a rather thinner latex,[32] and there is no reason to suppose the chemical or physical condition of the caoutchouc should vary. Whitby's figures show that there is little difference, if any, between rubber from young trees (five years old), and old trees (fifteen years old), whether the rubber be made up in the native Brazilian form, smoked in layers, or in the usual plantation form of smoked sheet.

Properties of Rubber.

I. I. Ostromyslenski[33] has suggested two new constants for the classification and evaluation of caoutchouc, natural or synthetic. To bodies which exhibit the "elastic" or "caoutchouc" state he gives the name of "resinoids." The constants refer to the limiting temperature for the elastic state of the given caoutchouc. The lower temperature is termed "the temperature of elasticity"; below this caoutchouc becomes hard and inelastic. The higher temperature is termed the "fatal temperature." These constants are measured by determinations of the properties, such as viscosity, density, etc., in colloidal solution. How these results are obtained is not clear. One would have thought that the time factor would have had to be taken into consideration. Thus in one example Ostromyslenski gives –20° C. as the elasticity point of natural caoutchouc, while it is well known that exposure to quite moderate cold (above 0° C.) will "freeze" rubber in the course of a few weeks. Similarly with the fatal temperature, long heating at a moderately high temperature will produce a similar effect to a short exposure at a higher temperature.

W. A. Caspari[34] has investigated the caoutchouc-benzene-alcohol and the caoutchouc-benzene-acetone systems. He concludes that caoutchouc is practically insoluble at 20° C. in mixtures containing 43 volumes or more of absolute alcohol or 80 volumes or more of anhydrous acetone to 100 volumes of benzene. A very small excess of precipitant serves to precipitate the whole of the caoutchouc; hence caoutchouc cannot be separated into components by fractional precipitation.

D. Spence and G. D. Kratz[35] have studied the swelling of rubber in organic solvents. They state that mechanical treatment renders the rubber incapable of swelling. Circular discs of raw rubber were immersed in various solvents. The solvents may be placed in the following order according to the volume of liquid absorbed by one gram of caoutchouc when swollen to the maximum extent:—(1) Carbon tetrachloride, and chloroform, (2) carbon bisulphide, (3) benzene, toluene, and xylene, (4) ether.

P. Bary[36] has studied the velocity of solution of liquids in rubber and gives a list of solvents in order of velocity. The order appears to be the same as that deduced by Spence and Kratz; thus these are values of p_s (the weight of liquid in a unit weight of rubber corresponding to the saturation of the rubber in the liquid):—Chloroform, 0·940; carbon bisulphide, 0·916; xylene, 0·849; benzene, 0·840; ether, 0·718, etc.

K. Gorter[37] has studied the effect of exposure to light of rubber in sealed tubes filled with hydrogen, carbon dioxide, air, and oxygen. The rubber only becomes tacky in the last two gases, and consequently he concludes that tackiness is caused by oxidation. The maximum increase in weight observed was 3 %.

Properties of Vulcanized Rubber.

In an interesting paper on rubbered balloon fabrics,[38] G. Barr states that these fabrics rarely leak less than five or six litres per square metre per 24 hours, while prepared oiled silk and goldbeater skin rarely leak more than $\frac{1}{5}$ litre. In addition the weight of the rubber fabric is greater. Nevertheless, it is preferred on account of its pliability, freedom from tackiness, ease with which joints are made, possibility of combining two or more plys by rubber layers and, finally, cheapness of a cotton in contrast to a silk fabric. The paper gives a full account of the properties of rubbered fabrics and the methods of testing. The permeability of rubber to gases is usually attributed to the solubility of gases in rubber. V. Rodt,[39] however, ascribes the rapid diffusion of CO_2 through a rubber septum to the high solubility of the gas in water

combined with the "hygroscopic" nature of rubber. He shows that loss of CO_2 takes place much more slowly when the gas and surrounding atmosphere are dry and that rubber thread in moist CO_2 takes up 6·12 % of moisture and 0·08 % of CO_2.

A reference has already been made to the deteriorating effect of alkalies on raw rubber after the rubber is vulcanized. The effect of alkalies and acids on rubber has also been investigated by W. G. Martin.[40] The matter comes prominently before manufacturers owing to the use of acids and alkalies in "reclaiming" processes and the difficulty of removing them completely afterwards. A mixing of rubber, zinc oxide, and a limited amount of sulphur (5 % calculated on the rubber), was chosen as particularly suitable for comparing the vulcanizing properties of rubber. Caustic soda was added to this mixing in proportion from $\frac{1}{4}$ up to 5 %. The results showed, taking one cure, an increase in breaking load and resistance to stretching, both curves showing maximum figures at 0·5 % of alkali. With larger proportions of alkali both cures fell away, and with 1 % of alkali the breaking load was practically nil. Identical results were obtained when zinc oxide was replaced by inert barytes. The effect of acid is in all cases to lower the breaking strain and resistance to stretching—the effect of $\frac{1}{8}$ % of sulphuric acid is distinctly noticeable to the feel. It is pointed out that if reclaim containing acid or alkali be added to a mixture containing a proportion of new rubber, this latter must be affected and a variation in cure will result. White substitute may also contain traces of acid, and it is usual to counteract this with small quantities of magnesium carbonate; in fact, most rubber mixings contain a proportion of some basic mineral substance, so that traces of acid are perhaps less dangerous than traces of alkaline substances.

Physical Tests on Vulcanized Rubber.

P. L. Wormeley[41] has studied the effect of change of temperature on some physical constants of vulcanized rubber. It has been recognized for some time that the temperature affects tensile determinations, so that it is advisable to keep the temperature of the testing room as constant as possible. Wormeley carried out experiments between 9° and 35° C., and found that "elasticity" was the most sensitive to changes of temperature and the ultimate elongation least so, the tensile strength occupying an intermediate position. By "elasticity" is meant the "set" measured after stretching the specimens in strip form for a definite period. It is therefore a measure of the recovery after stretching, and is more usually termed "recovery" or "subpermanent set." The specimens were kept stretched for one minute and given

one minute for recovery. The author, however, admits that the method chosen is arbitrary, as apparently the elongation varied with different compounds on an arbitrary basis. It would certainly appear more reasonable to have applied a constant load; the elongation would then have been conditioned by the composition of the rubber compound. Wormeley finds that, although the effect of temperature varies markedly with different types of vulcanized rubber, the tendency is always to give a smaller "set" the higher the temperature at which the test is made. If, however, the specimens had been subjected to the same load instead of elongated to the same extent, it is easy to imagine that the results might have been reversed. The softening effect of the heat is demonstrated by the increased ultimate elongation. This, however, is small as compared with the decrease in "set." The breaking load is also influenced to an appreciable extent, the figure being lower at higher temperatures, but the variation is least with high grade specimens.

At present the mechanical testing of vulcanized rubber is in no way standardized. A number of machines were devised by K. Memmler and his associates at the Materialprüfungsamt, Berlin.[42] Of these the most important is the machine for carrying out tensile tests. After exhaustive experiments with strips of rubber of various shapes and compositions, they abandoned the use of strips altogether and adopted the ring-shaped test piece. This had been previously adopted for the purpose[43] in preference to strips, even when the latter were cut with wide ends to prevent tearing in the grips. If one may judge, however, from this paper by Wormeley and from another paper by D. E. Douty,[44] the strip method is preferred by rubber chemists in the United States. The machine employed in the U.S. Bureau of Standards consists of a pedestal carrying a spring dynamometer to which is attached one grip to take one end of the rubber strip. The lower end of the strip is held by a similar grip, which is pulled down by suitable gearing so as to stretch and eventually break the specimen strip. A special form of construction is claimed for the grips of which "the pressure portion consists of a series of eccentrically drilled discs, with knurled edges, so mounted as to automatically tighten as the tension increases. The discs work independently, but by means of a small piece of rod passing through them and fitting loosely, are operated together in placing or removing the specimen." It is claimed that there is no cutting or tearing action, and it would certainly seem to be an advance on previous forms of grips with rounded, smooth, or corrugated surfaces held by set screws. In this new form of grip the pressure applied to hold the rubber in position will automatically correspond with the

tension on the strip, so that only just sufficient pressure is applied to keep the rubber strip from slipping in the grip. If the difficulty of satisfactorily gripping the ends of a test piece of rubber strip has been successfully overcome, it would certainly appear to offer some advantages over the ring-shaped test piece. In this latter the tearing action, or crushing of the rubber at the points of the ring at which the tension is applied, has been largely overcome by stretching the ring between pulleys in the place of smooth hooks, one of the pulleys being made to revolve while the ring is being stretched. The movement of the ring equalizes the strain, and any crushing is but momentary. The idle pulley, however, is not frictionless, so that strain is not perfectly equalized over the length of the ring. There is, however, a still greater error introduced owing to the test ring having an appreciable thickness in relation to its periphery. It is obvious, as the writer first pointed out,[45] that the more the rubber stretches the thinner the ring becomes. As the volume of the rubber remains practically constant during stretching, portions of the rubber on the external surface of the ring will be stretched to a lesser extent than the rubber on the internal surface. This results in a variation in the tension in different parts of the ring, causing it to tear and rupture at a lower strain than would otherwise be the case. On this account, thin rings give a higher breaking load for the same cross-sectional area than thick rings. Indeed, as Memmler has shown,[42] it is possible, by reducing the thickness of the ring from 6 mm. to 2 mm., almost to double the breaking strain, although the ultimate elongation was not affected. On the other hand, strip-shaped test pieces must be made wider at the ends where they are gripped to ensure rupture outside the grips. This has the disadvantage that the rubber tends to flow from the thick to the thinner parts of the strip, which tends to increase the tensile figures. Douty[44] states that the elongation, as determined by the ring method, is only 85 % of that by the strip method, while Memmler asserts that the type of grip with eccentrics is not effective for use with high grade rubbers. Whatever the method of testing, it is these high grade rubbers containing a high percentage of caoutchouc and a small percentage of minerals which offer the greatest difficulties in testing. These are the softest and show the highest ultimate elongation; they frequently stretch to ten times their original length before breaking. The highest type of this class is that compounded of raw rubber and sufficient sulphur for full vulcanization without any other ingredient. From this point of view it is unfortunate that this type has been chosen for vulcanization experiments, as, with every precaution, duplicate rings give appreciable variation in breaking strain; indeed, Eaton

—whose work has already been referred to at some length—now prefers to be guided by the load stretch curve rather than the breaking load in arriving at a valuation of the properties of the vulcanized specimen. He has not, however, shown that his load stretch curves alone are sufficiently characteristic to define the tensile properties of the rubber, and it appears not impossible that practically identical load stretch curves may be given by two specimens showing different breaking strains or, from another point of view, a specimen giving a high resistance to stretching does not necessarily possess a high breaking strain. In any case, comparison can only be made between rubber specimens compounded on the same formula. It is evident that much detailed work is necessary before any standard method of testing can be evolved. Any attempt to arrive at a standard as advocated in some quarters is premature. Douty[44] also describes the apparatus used by the U.S. Bureau of Standards for various other tests, including friction tests on rubber hose, belting, etc., but which do not present any particularly novel features.

In the same collection of papers P. Schidrowitz[46] outlines a method of vulcanization tests whose prime object is the determination of rate of cure or "curing capacity" of different specimens of raw rubber. After emphasizing the necessity of keeping constant all factors in the preparation and vulcanization, the only remaining variable is the time during which the specimen is heated for the purpose of vulcanizing. By the correct adjustment of the time of heating one arrives at a "perfect cure" for the given conditions. Having ascertained the perfect cure, the rubber so vulcanized is subjected to appropriate tensile tests. It is not possible to arrive at the perfect cure without one or more preliminary vulcanizations. Once, however, these are made, the rest is merely a matter of calculation, although a final check on the preliminary results may be carried through at the perfect cure previously arrived at by calculation. The method of calculation is given very briefly and with insufficient details for explanatory purposes. We are told that the calculations are based on load-stretch curves. These, "referred to Cartesian co-ordinates, have been found by E. Hatschek to correspond to

$$y = a - b \,.\, \sin \alpha$$
$$x = n\,(a \,.\, \cot \alpha - b \,.\, \cos \alpha)$$

In any set of curves a and b vary according to the state of cure and n is a constant independent of the state of cure." "Any curve in which $a = b$ corresponds to a theoretical ideal balance of properties" and "has been found by experiment" to give "the best results as

regards tensile properties, etc." This curve, therefore, corresponds to the best or perfect cure.

A large number of figures are given in the paper which are summarized at the end, from which we gather that the variation in rate of cure as determined by this method may be very considerable. Thus, plantation unsmoked sheet may vary from 1 hour to $4\frac{1}{2}$ hours, that is to say, one specimen under the constant conditions of the experiment may take only one hour for the "perfect cure" while another specimen may require $4\frac{1}{2}$ hours under the same conditions. Although the author has been careful to insist on uniform conditions in vulcanization and testing, he does not mention what interval, if any, was allowed to elapse between vulcanization and the actual tests. This interval would have an appreciable effect on the results. The whole system appears to be based on theoretical foundations, namely, the equivalency of the values of a and b in the equations given above. No attempts have been made to supply any form of practical control or to show that specimens which have been given the "perfect cure" will age satisfactorily.

Quality and Uniformity of Rubber.

When contrasting plantation and Brazilian Para rubber, reference has been made to the matter of uniformity. This is of particular importance as regards rate of cure, because, if a compounded rubber be overcured, eventual deterioration takes place. A specimen may show some improvement for a time, but later on deterioration sets in and, if the overcuring is pronounced, the vulcanized rubber becomes "perished," that is to say hardened and brittle. This deterioration must not be confused with suncracking or perishing due to exposure to bright light, excessive heat, etc. Moreover, some goods are of such poor quality that a lasting and satisfactory vulcanization cannot be obtained. Overcuring applies particularly to medium and better grade rubber goods which are expected to last for two or three years without marked deterioration. It is obvious that, if the rate of cure varies, the manufacturer may have difficulty in curing to the right degree and bringing out the best qualities of his compounds without overcuring them. This want of uniformity as regards rate of cure is regarded by some as the greatest drawback to the use of plantation rubber by manufacturers. This view was recently put forward by Williams,[47] who quotes examples from manufacturing practice of adjustments in time of vulcanization up to 100 %, but it is not clear whether the adjustments became necessary on replacement of wild rubber by plantation rubber or for what cause. They all represent a considerable

increase in time or temperature of vulcanization and, as plantation rubbers are known to cure faster than most others, it would appear that the examples refer only to factory conditions. It is admitted that when the conditions are correctly adjusted, much better results are obtained than with medium wild qualities, but it is stated that plantation rubber is not equal to native Para when put into use and subjected to considerable fatigues. This represents one view of plantation rubber in ordinary manufacture. The reverse aspect is presented to us by another manufacturer in the same publication. J. M. MacLulich[48] is of opinion that any failure to obtain the best results with plantation rubber is due to lack of adjustment in manufacturing conditions, as methods adapted to wild rubbers require modification. With railway buffers he obtained a 6-ton load with plantation rubber as against a $4\frac{1}{2}$-ton load with fine hard Para. He further states that "there are at least forty brands of plantation rubber of which you can take any one and get the same result, provided you are careful in manufacture," and that wild rubber "varies to a far greater degree than plantation rubber."

With such widely divergent views as to the quality and uniformity of plantation rubber it will perhaps be wisest to suspend judgment or to take a middle course. Two facts, however, stand out which cannot be gainsaid: (1) Plantation rubber is being used in quantities which are increasing at a rapid pace (*see* statistics of output), to the detriment of wild rubbers. (2) Fine hard Para, the output of which remains stationary, still fetches a marked premium in the market over all plantation grades.

Vulcanization.

Much work on this subject has recently been published by Ostromyslenski,[49] who claims to have discovered new agents for vulcanization which can replace sulphur. Thus "complete vulcanization" is obtained by heating a mixture of Para rubber 100 parts, litharge 8 parts, and 1.3.5-trinitrobenzene 4 parts, in a vulcanizing press for 45 minutes at 45 lb. steam pressure. Various nitrobenzenes can be used, but the symmetrical trinitrobenzene is the most effective. It is claimed that 0·5 % of this substance is as effective as 6 % of sulphur when compounded with natural Para rubber. The nitrobenzenes may be replaced by various other fatty or aromatic compounds such as nitronaphthalenes, picric and picramic acids, picryl chloride, nitro-cyclohexane, etc. In a table of experimental data accompanying the paper it is noteworthy that, except in three instances, the rubber is compounded with litharge. In one instance in which litharge was

omitted, vulcanization did not take place, but in another, satisfactory vulcanization was obtained with as little as 0·8 % of trinitrobenzene in the absence of litharge. In the third case, litharge is successfully replaced by magnesia. H. P. Stevens made some preliminary confirmatory experiments but could not obtain vulcanization with a mixture of rubber and dinitrobenzene only.[50] It should also be noted that most of Ostromyslenski's experiments were carried out on such small quantities as 10 grams of rubber, and the condition of the product is only briefly described, such as "vulcanization complete" or "somewhat over-vulcanized," etc. No figures are given or analyses of the vulcanized products. In another paper there is described the vulcanization of rubber by means of peroxides or peracids in the absence of sulphur. The reagent mostly employed was benzoyl peroxide, but it was found that litharge, magnesia, and other metallic oxides, which promote vulcanization in the case of the nitrocompounds, retard vulcanization in the case of the peroxides. The same applies to the amines, which usually act as accelerators. Vulcanization was complete with 1 % of the peroxide on the weight of the rubber and unnecessary excess of the reagent must be avoided, otherwise the tensile strength will be negligible, presumably owing to "over-vulcanization." When vulcanized at a high temperature, after-vulcanization is very pronounced. Benzoyl peroxide may be replaced by perbenzoic acid and probably by ozone, ozonides of caoutchouc, etc., but barium peroxide produces no trace of vulcanization.

In some later papers Ostromyslenski[51] describes a new method for cold vulcanization; the vulcanizing agent may be sulphur, trinitrobenzene, or benzoyl peroxide. This result is obtained by incorporating with the rubber a primary or secondary aliphatic amine in conjunction with a metallic oxide. These latter substances act so promptly as accelerators that vulcanization takes place at ordinary atmospheric temperatures. The vulcanization is complete in from a few weeks to three months. Alternatively the process is accelerated by very gentle heat. Thus a mixture of caoutchouc, 50 grms.; sulphur, 2·5 grms.; piperidene piperidyldithiocarbamate, 0·5 grm.; and zinc, magnesium, or lead oxide, 5 grms., when heated to 40°–60° C. for ten to forty minutes, at first suffers no apparent change, but on standing is completely vulcanized in ten to forty-eight hours. If nitrobenzene be substituted for sulphur, no special catalyst such as the amine mentioned above need be used, but metallic oxides are necessary for rapid vulcanization. It is only necessary to give the mixture a short preliminary heating at 50°–60° C., which can be effected by preparing it on hot rolls, to ensure that "vulcanization" will proceed afterwards in the cold. Similar results are obtainable with benzoyl peroxide, except that the metallic

oxides must be omitted, as they retard vulcanization. The discovery of substances which can replace sulphur in vulcanization is of a character to rank with those of Goodyear and Parkes, should it be found capable of commercial application. The term "vulcanization" is, however, a little vague when applied to a change in physical properties without any definite chemical data to correspond. The changes produced by vulcanization with sulphur can be followed not only by means of physical tests, but by determining the proportion of sulphur not extractable by acetone (the so-called "combined sulphur"). When vulcanization has been brought about by trinitrobenzene or benzoyl peroxide we require to know whether, analogously to sulphur, part of these reagents remains "combined" with the rubber. We also require measurements of the physical qualities of the "vulcanized" rubber before we can decide how far this "vulcanization" without sulphur is comparable with ordinary vulcanization with which we are familiar. Ostromyslenski's work does not provide us with evidence of this nature. That he has obtained rubber in a condition apparently similar to ordinary vulcanized rubber may be admitted, but further research is necessary to ascertain whether the properties of his "vulcanized" rubber are really economically comparable with rubber vulcanized with sulphur. The products obtained with trinitrobenzene and benzoyl peroxide exhibit to a marked degree the tendency to after-vulcanization. If this cannot be controlled, such rubber will not age satisfactorily. For the same reason, the method of vulcanization in the cold or at a relatively low temperature may not be of practical value. Nevertheless, it may be possible so to control the initial heating that the vulcanization proceeds only to a certain degree and then gradually comes to a stop, as this phenomenon is similar, although less pronounced in the case of rubber vulcanized with sulphur under ordinary technical conditions. The physical qualities continue to alter for some time after the vulcanizing operation is complete, and then gradually come to a stop, provided the conditions of the vulcanizing operation (curing) were properly adjusted in the first instance. If, however, the heating was a little too prolonged, or the temperature too high, the changes due to the after-vulcanization effect do not gradually cease, but rather gain momentum, so that the product gradually loses its tensile properties, becomes brittle, and eventually "perishes." Ostromyslenski appears to have realized the danger of "over-vulcanization" with benzoyl peroxide, for he states that the "vulcanization" with this reagent requires "increased attention or skill in the operator." Whatever be the final verdict, Ostromyslenski has opened up a new branch of rubber chemistry, and possibly also of rubber technology.

In a subsequent paper Ostromyslenski[52] discusses the "vulcanization" with ozone, which he states depends on the preliminary formation of caoutchouc ozonide. The chemist familiar with the destructive action of ozone on rubber tubing may evince surprise at the use of this destructive agent for the constructive operation of vulcanization. There is, however, no reason why ozone, under properly controlled conditions, should not have a vulcanizing effect. All such changes present no difficulties to those who regard vulcanization as primarily a physical change, a pectination of caoutchouc. These researches throw some light on the rival physical and chemical theories of vulcanization. Perhaps the weight of current opinion favours a combination of the two. Spence, who made exhaustive researches on the mechanism of vulcanization,[53] arrived at the conclusion that the first changes were of a physical nature — namely, the adsorption of the sulphur by the rubber; subsequently a chemical reaction took place with the formation of a caoutchouc-sulphur complex. Ostromyslenski takes a different view.[54] The first change is a chemical reaction which takes place between the vulcanizing agent and a very small portion of the caoutchouc. The second is the "adsorption or swelling of the unchanged caoutchouc into the product of this chemical reaction." Theoretically, however, he thinks it may be regarded as exclusively a physical process, for the compound of caoutchouc may first be isolated and then incorporated with several times its weight of caoutchouc.

Analogously with the production of "soft rubber" by the vulcanization with trinitrobenzene, etc., Ostromyslenski claims to have produced the counterpart of hard rubber or vulcanite (ebonite) by means of various halogens. The initial stage consists in the formation of a caoutchouc halogenide, which may first be prepared. This is subsequently incorporated with the caoutchouc. Thus we may first prepare caouprene chloride, and the amount of caoutchouc for incorporation with this may be reduced to 7–10 parts per 100 parts of the chloride, thus considerably reducing the cost of the vulcanite. The product has a black colour, takes a good polish, and is a non-conductor. Curiously, however, it is stated that it can be scratched with the nail, in which case it must be much softer than ordinary ebonite.

S. J. Peachey[55] claims to have produced a plastic or solid material which can serve as a substitute for celluloid or leather by treating indiarubber with chlorine. The reaction is carried out in carbon tetrachloride or other suitable solvent. The product formed is separated from the solvent and incorporated with camphor or other filler.

Another method of vulcanizing has been described by A. Helbronner and G. Bernstein.[56] The destructive action of light on vulcanized

rubber is well known. V. Henri[57] carried the matter somewhat further, using the ultra-violet rays from a mercury vapour lamp. Ostromyslenski has shown how ozone, although destructive to rubber, can be employed as a vulcanizing agent. Similarly ultra-violet rays can be used for the same purpose.[56] The rubber is masticated, and the solution may contain from 1–5 % of rubber. The sulphur is incorporated, and the solution placed in a hopper, from which it passes to an endless band, moving on rollers. In its passage it is exposed as a thin layer to the ultra-violet rays from a quartz mercury vapour lamp, which is surrounded by a cold water jacket. The solution is removed by a scraper. The effect of the exposure is to cause a part of the sulphur to "combine" with the rubber, but the percentage calculated on the rubber (coefficient of vulcanization) is much smaller than in the case of ordinary hot vulcanized rubber goods, amounting to only 0·6 %. An increase in the percentage of sulphur beyond a certain point results in a diminution rather than an increase in the combined sulphur, and a corresponding diminution in tensile properties. It is also interesting to note that the vulcanizing effect may continue after the exposure to the ultra-violet rays, so that this vulcanizing agent behaves similarly to hot vulcanization with sulphur, trinitrobenzene, benzoyl peroxide, etc.

One would have expected the vulcanized rubber to be precipitated from the solution, as ordinary vulcanized rubber is insoluble in the usual solvents for raw rubber. It is found, however, that no precipitation takes place, the solution merely increasing in viscosity one-hundredfold or more. Once, however, this solution has been allowed to dry down the rubber is no longer soluble. The authors claim that the solution should have considerable technical value. The authors test the strength of the vulcanized solution by the ordinary method of solutioning together strips of cloth and determining the force required to separate them. The strength of the vulcanized rubber solution so prepared is much greater than that of the raw rubber. Such conclusions must, however, be accepted with some reserve, because so much depends on the type of raw rubber and the degree of mastication. It is well known that pale crepe rubbers produce solutions of very poor cementing value, whereas fine Para and plantation smoked sheet give good cementing solutions, provided the mastication is carried to the right degree. The results demonstrate that the vulcanizing treatment improves the cementing strength of the rubber, but do not show that the treated rubber has a greater cementing power than fine Para or smoked sheet properly masticated. No data are supplied as to the properties of the rubber when dried down in the form of films; it would be interesting to learn if these films have a tensile strength

comparable with rubber films vulcanized by the ordinary methods and if they show the same indifference to changes of temperature.

Some valuable experimental data have been obtained by H. Skellon[58] as the result of vulcanizing fine hard Para rubber compounded with 3–50 % of sulphur. The sheeted compounds were wrapped in cloth round a mandrel and vulcanized for various periods for one and a half up to nine hours at 140° C. The results, calculated as percentages of "combined" sulphur to rubber taken, present some interesting features when displayed in the form of a graph. Thus, by taking the figures for combined sulphur as ordinates, and those for the total sulphur as abscissæ, we obtain a series of curves for each cure, all of which show maximum points for the percentage of combined sulphur; in other words, for any cure the addition of sulphur beyond a certain figure tends to reduce the percentage of combined sulphur. Judging from the lie of the curves, the maximum proportion of combined sulphur with an infinitely long cure would reach 32 %. From previous experiments[59] the author finds that at the commencement of vulcanization a mix containing 10 % sulphur and 90 % Para was a saturated solution of sulphur in rubber, and, curiously, the maximum points on the lowest curves (cures at half to one and a half hours) are with mixings containing 10 % sulphur. In the discussion which followed the paper it was suggested that these results showed that no advantage as regards rate of vulcanization would be obtained by increasing the proportion of sulphur beyond 10 % calculated on the rubber. This, however, could only apply to simple mixings of rubber and sulphur without metallic oxides, which are present in the great majority of technical mixings. Further, none of Skellon's cures give a properly cured rubber at the maximum point of the curves, to judge by the percentage of combined sulphur. A cure of two or two and a half hours would be necessary, and the maximum of combined sulphur would then fall at a point somewhat exceeding 10 % of total sulphur calculated on the rubber.

G. D. Kratz[60] has made comparative vulcanizing tests on portions of the same compound, consisting of rubber, sulphur, and zinc oxide at various pressures. The state of cure was judged by rough hand tests and the correctly cured specimens subjected to tensile tests. The steam pressures in the vulcanizer varied from 36 to 85 lb., and the increase in pressure necessitated a corresponding reduction in length of cure from 120 to 8 minutes. Ten specimens were tested, and the results shown vary in an irregular manner from approximately 2500 to 3000 lb. per square inch tensile strength, and 725 to 800 % elongation. Ageing tests were made, extending over four months, but figures of these tests

are not given. The conclusion is drawn that within reasonable limits the temperature at which a rubber mixture is vulcanized in no way affects the final quality. This may be so. It is well known in practice that temperature and time of vulcanization are mutually adjustable within certain limits, but a more elaborate series of experiments will be required to show that ageing qualities are not affected by the temperature of vulcanization. Four months is not long enough, and would only reveal very marked over-vulcanization.

H. P. Stevens[61] has studied the effect of varying the proportion of litharge in a mixture composed of rubber 100 parts and sulphur 5 parts. During vulcanization, part of the sulphur (1) reacts with the litharge to form lead sulphide and sulphate, and another part (2) enters into "combination" with the rubber, while a third part (3) remains "free" or capable of extraction with acetone. The distribution of the sulphur was determined by analysis of the compounds vulcanized under the same conditions. Theoretically, seven parts of litharge require one part of sulphur for complete reaction; the rubber was therefore compounded with 7, 14, etc., parts of litharge for every 5 parts of sulphur. The best vulcanized product showing the highest percentage of "combined" sulphur was obtained in the mixing containing 17·5 parts of litharge, which would require 2·5 parts of sulphur for full saturation. With larger proportions of litharge, the rubber appeared undercured, and possessed a lower vulcanization coefficient, showing that so large a part of the sulphur was claimed by the litharge that insufficient was left for full vulcanization of the rubber. The proportion of free sulphur diminished with the increase in the litharge and became almost negligible in the mixing with more than 28 parts of litharge.

J. Bastide[62] describes the use of a solvent of sulphur in a mixing with rubber to obtain a better distribution of the sulphur and reduce the proportion necessary for vulcanization. As, however, the "solvents" used are amines such as methylethylphenylene diamine, it would appear likely that the advantage claimed is brought about by the "accelerating" action of this substance rather than by its solvent action on rubber. One may even suggest that there is possibly some connection between an accelerator and its solvent action on sulphur.

Accelerators.

The list of organic substances which have been found to accelerate vulcanization grows steadily. The list now includes amines, particularly diamines, ammonia compounds, anilides, and compounds of aniline and other bases with carbon bisulphide, piperidine and quinoline, and their derivatives, anthraquinine, albumens, etc. Recent additions by

S. J. Peachey include compounds formed by the interaction of aromatic amines with aliphatic or aromatic aldehydes, or of an aromatic aldehyde with ammonia, such as formaldehyde-aniline, hydrobenzamide,[63] and paranitrosodiphenylamine.[64] Bayer and Co.[65] claim all bases or basic ammonium derivatives having a dissociation constant greater than approximately 1×10^{-8}. As examples are quoted *p*-phenylenediamine, aldehyde-ammonia, benzylamine, naphthylenediamine, ammonium borate, and sodium amide. One would imagine that so broad a claim would cover a very wide range of products, including some already patented. Of these numerous patented products, we have heard very little until recently as to their practical application in the rubber factory. It must not be forgotten that the use of mineral accelerators in the form of litharge, magnesia, etc., is almost as old as the industry itself. The question may be raised as to the value of organic accelerators in the presence of litharge and magnesia, which form a part of the ingredients of the great majority of rubber goods. Most of the patentees substantiate their claim to the use of certain organic compounds as accelerators by reference to the effect produced on a mixing of Para rubber with 10 % of sulphur. Such a mixing is of little or no importance from the manufacturing standpoint; pure rubber thread is perhaps the only important example of this type. Moreover, this mixing is probably the most sensitive of any to conditions affecting the rate of cure. The mechanism of the action of amines as accelerators is explained by Ostromyslenski by assuming the formation of an unstable thiozonide.[66]

R. Ditmar[67] points out that a combination of two catalysts may be more effective than the sum of each individually. The effect is not proportional to the quantity used, and large quantities may reverse the effect of smaller ones.

Synthetic Rubber.

The outlines of this subject do not grow simpler with development. The bodies synthesized correspond not only to the supposed constitution of natural *Hevea* caoutchouc but to various analogues of this. Of recent work the greater part is contributed by Ostromyslenski.[68] There are also patent specifications, as that dealing with the polymerization of β-myrcene.[69] In this process isoprene yields β-myrcene when the former is allowed to stand alone or in the presence of a catalyst or heated to a temperature not exceeding 150°C. Polymerization of β-myrcene to yield caoutchouc is brought about either spontaneously or by the action of heat, light or electricity either with or without a catalyst. A number of examples are given both of the

production of β-myrcene from isoprene, and the polymerization of the β-myrcene thus produced. In the simplest instances isoprene is heated for ten days at 80°–90° C. in a closed vessel, the mixture of products is then heated with 20 % of sodium wire at 70°C. These various processes appear to differ from previous ones merely in the separation of the isoprene treatment into two stages, β-myrcene being the intermediate substance formed. From one of Ostromyslenski's papers[70] we learn that the name β-myrcene is given to "an open-chain, myrcene-like hydrocarbon, $C_{10}H_{16}$, which contains three ethylenic linkings, two of them in conjugated positions." It is a colourless, mobile liquid, soluble in all the ordinary organic solvents, and boils at 63°–63·5° C. under 20 mm. pressure. The conversion into normal isoprene-caoutchouc is quantitative when β-myrcene is heated at 60°–70° C., with sodium and barium peroxide. Under similar circumstances, isoprene itself would yield an "abnormal" caoutchouc. In a further communication, reference is made to the work of Steimmig.[71] It will be remembered that Steimmig, in certain criticisms of Harries' work, showed that the decomposition of the ozonides of synthetic caoutchouc prepared by the Bayer patents produced succinic acid and acetonylacetone in addition to lævulinic acid and aldehyde, while natural caoutchouc produces the two latter only. Synthetic caoutchouc must consequently consist in part of 1.6-dimethylcyclo-octadiene, natural caoutchouc being the corresponding 1.5-derivative. Ostromyslenski claims that his caoutchouc from β-myrcene differs from all previous synthetic caoutchoucs, being perfectly identical with natural Para caoutchouc. It should, however, be noted that Harries ascribes Steimmig's results to the use of impure isoprene. Ostromyslenski draws attention to the rather suggestive similarity of atom grouping which exists between β-myrcene and such plant derivatives as geraniol, linalool, nerol, etc., arguing that β-myrcene may form the intermediate stage in the production of caoutchouc by the tree.

Ostromyslenski has also studied the polymerization of diolefines and states that much of the work published on this subject since 1911 is inaccurate.[72] He describes the behaviour and properties of caouprene bromide and its reduction to erythrene-caoutchouc and the isomeric caouprene, a viscous liquid or an amorphous elastic mass. By heating to 50°–60° C. with benzoyl peroxide, it is converted quantitatively into normal erythrene-caoutchouc. The regeneration of caoutchouc from the tetrabromide has been studied by Kirchhof.[73] Two atoms of bromine can be removed with alcoholic potash at 100° C., but the removal of the remainder of the bromine requires a much higher temperature, and the product is not identical, but isomeric, with the

original rubber. C. Harries and E. Fonrobert[74] have studied the regeneration of rubber from the hydrochloride. Here again the regenerate was not identical with the original caoutchouc. F. E. Matthews and E. H. Strange[75] have patented the use of liquid SO_2, which they claim increases the viscosity of the caoutchouc formed by treating butadiene with sodium. It will be remembered that these chemists discovered the polymerizing effect of sodium on isoprene, although it was found later that the product so obtained was not identical with that produced by polymerization with other reagents. The Badische Co.[76] have patented the use of certain organic acids for treatment of such synthetic caoutchoucs as that referred to above as obtained by the action of sodium on butadiene. F. Bayer and Co.[77] have patented the use of liquid sulphur dioxide, or a solution of sulphur dioxide in a solvent such as toluene for separating butadiene from other valueless gases. The butadiene is absorbed quantitatively, and is recovered by removing the sulphur dioxide by distillation or by treatment with bases. A. Heinemann[78] has also patented the use of SO_2 on butadiene or isoprene dissolved in acetone. The white precipitate which separates is compressed and yields a substance of the nature of guttapercha or balata. H. Stern[79] has patented the treatment of aliphatic ketones with fuming sulphuric acid, by which means a rubber-like hydrocarbon is produced. It is curious to note how all these patents are based on the action of sulphur dioxide.

Ostromyslenski[80] also describes new methods of preparation of a number of unsaturated hydrocarbons used in the production of various synthetic caoutchoucs, including divinyl, isoprene, piperylene, dimethyl-erythrene, and conversion of cyclo-butane derivatives into erythrene. Another paper deals with the analysis, purification and reactions of isoprene,[81] while a third[82] describes a simple method for the synthesis of butadiene by passing a mixture of ethyl alcohol and acetic aldehyde vapours over heated alumina at a temperature of 360° to 460° C.

Analysis of Vulcanized Rubber.

For the analysis of vulcanized rubber goods portions must be rolled very thin or reduced to a fine state of division previous to acetone extraction. This is usually performed on a small power-driven roller machine. For analysts, L. Archbutt[83] recommends a small pair of adjustable grooved rollers geared 3:2 or with one roller fixed. The action is a grinding or cutting one, according to the adjustment. R. Wheatley and B. D. Porritt[84] prefer a revolving cylindrical file or rasp 1 inch in diameter with cutting edges parallel to the axis. The

machine is driven by a $\frac{1}{8}$ h.p. motor, and the speed can be varied. Either machine is said to reduce all commercial grades to a fine state of division. Although some heating takes place, this is found to have no effect on the analytical results, but care must be taken to avoid oxidation of the finely divided material.

Several recent papers deal with the estimation of sulphur in vulcanized rubber. R. Gaunt[85] has described a combustion process. The rubber is burnt in a current of oxygen and the sulphur dioxide is absorbed in a solution of hydrogen peroxide, the sulphuric acid formed being then estimated in the ordinary manner. A. Hutin[86] describes a variation of the ordinary nitric acid oxidation process (Henriques' method) for determining total sulphur by concentrating the nitric acid solution and mixing the syrup with magnesia to a stiff paste before ignition. J. B. Tuttle and A. Isaacs[87] have made comparative tests of various methods for the determination of total sulphur, and obtained the most satisfactory results by the method of C. E. Waters and J. B. Tuttle,[88] which consists in a modification of Henriques' method, the oxidation being carried out with nitric acid saturated with bromine. Stevens[89] has devised a new method for the estimation of sulphur present in the form of metallic sulphide. The rubber is swollen with ether or other solvent, in which condition it is readily permeable to hydrochloric acid. The sulphides are thus decomposed and the sulphuretted hydrogen is driven off by heating and precipitated as lead sulphide and estimated iodometrically. The sulphur present as sulphate may also be extracted and estimated. J. B. Tuttle[90] has described a method for the separate estimation of barium sulphate and carbonate in vulcanized rubber. The barium carbonate is first determined by igniting the rubber in a current of CO_2 and digesting the ground residue in a solution of ammonium carbonate to dissolve the barium carbonate, separating the barium sulphate and insoluble carbonates by filtration. After removal of the lead, the barium is estimated in solution as barium sulphate. The total barium is estimated by oxidation and the barium sulphate by difference. E. B. Phelps and A. F. Stevenson[91] have analyzed a number of rubber teats and children's toys. Those containing antimony were digested in 0·5 % lactic and hydrochloric acids for five days at 37° C., when in some cases appreciable amounts of antimony were dissolved. On rubbing in a mortar with fresh saliva acidified with lactic acid for $1\frac{1}{2}$ hours, two of the red rubbers yielded 0·2 and 0·6 mgrm. of antimony. The use of antimony in articles for infants is therefore condemned. This matter of the solution of toxic metals from vulcanized rubber has frequently been the subject of investigation, as in the cases of Codd's rings for aerated

beverage bottles, beer hose, etc., and results are conflicting. Much depends on the quality of the vulcanized rubber.

The Board of Trade published in Bulletin No. 81 a return of various rubber wares imported from and exported to Germany and Austria-Hungary during 1912 and 1913—that is to say, previous to the outbreak of war. The figures are of considerable interest, but marred by the absurdly literal translations of German terms. As examples we may quote:—"Hardened rubber," "rubber paste," "hardened rubber paste for dental use," "patent sheets," "inlaid wire"—expressions which convey no meaning to rubber manufacturers in this country not familiar with the German equivalent of the English terms for vulcanite, dental rubber, cut sheet, etc.

[1] *J.*, 1915, 93.

[2] Dunlop Rubber Co., Ltd., and E. Mosinger, Eng. Pat. 16096, 1914, *J.*, 1915, 843.

[3] Eng. Pat. 22138, 1914, *J.*, 1915, 1020.

[4] *Agric. Bull. Fed. Malay States*, 1915, **4**, 30; *J.*, 1916, 263.

[5] *India Rubber J.*, 1916, **51**, 713.

[6] W. G. Martin, *The Rubber Industry*, 1914, 205–210; *J.*, 1915, 725.

[7] *Agric. Bull. F.M.S.*, 1915, **4**, 28; *J.*, 1916, 263.

[8] *J.*, 1916, 493.

[9] *J.*, 1915, 989.

[10] *J.*, 1915, 501.

[11] F. Ripeau, *The Rubber Industry*, 1914, 124–9; *J.*, 1915, 291.

[12] *Preparation of Plantation Rubber*, 203.

[13] *Agric. Bull. F.M.S.*, **4**, 5; *J.*, 1916, 264.

[14] Whitby, *J.*, 1916, 497.

[15] J. G. C. Vriens, *Bull. Agric. Intell.*, 1915, **6**, 1064; *J.*, 1915, 1104. R. S. Algar, Eng. Pats. 7960 (1915) and 6215 (1914), *J.*, 1915, 806, 1105. S. Milne, Eng. Pat. 24680, Dec. 28, 1914, *J.*, 1915, 1020. J. Schadt, Eng. Pat. 12002, Aug. 19, 1915, *J.*, 1916, 479. W. G. ten Houte de Lange and C. Bosman, Eng. Pat. 10382, July 16, 1915, *J.*, 1916, 644. Compare also Wickham's process (Eng. Pat. 2627, Jan. 31, 1914, *J.*, 1915, 40) and earlier patents, particularly Eng. Pat. 7371 of 1907.

[16] N. W. Barritt, Eng. Pat. 3632, Feb. 12, 1914, *J.*, 1915, 368.

[17] *Bull. Agric. Intell.*, 1915, **6**, 1703–4; *J.*, 1916, 368.

[18] *Jour. Liverpool Univ. Inst. of Commercial Research in the Tropics*, No. 31, 1907; *J.*, 1907, 1287.

[19] *Kolloid Zeitschrift*, **11**, 61, 1912; **12**, 46, 1913; **14**, 91, 1914; *J.*, 1912, **31**, 1099.

[20] *Koll. Zeit.*, 1914, **14**, 262; *J.*, 1914, 653.

[21] *Ibid.*, 1914, **15**, 49–50; *J.*, 1915, 500.

[22] *Rubber Industry*, 1914, 144–148; *J.*, 1915, 435.

[23] *Agric. Bull. F.M.S.*, 1915, **3**, 186–194.

[24] *Ibid.*, 1915, **3**, 442 *et seq.*; *J.*, 1915, 263.

[25] *Rubber Industry*, 1914, 137–143; *J.*, 1915, 436.

[26] *Agric. Bull. F.M.S.*, **4**, 219; *J.*, 1916, 854.

[27] Beadle, Stevens, and Morgan, *India Rubber Journ.*, Aug. 2, 1913: S. Morgan, "The Preparation of Plantation Rubber," pp. 69 *et seq.*; Beadle and Stevens, *Le Caoutchouc et la Gutta Percha*, 1915, **12**, pp 8730–1, also *Rubber Recueil*, International Rubber Congress, Batavia, 1914, pp. 357–360; *J.*, 1913, 835.

[28] *Rubber Industry*, 1914, 291, also Stevens, 294–5; *J.*, 1915, 880.

[29] *Agric. Bull. F.M.S.*, **3**, 218 *et seq.*; *J.*, 1916, 263.

[30] *Preparation of Plantation Rubber*, 211.

[31] *Agric. Bull. F.M.S.*, **4**, 1-4; *J.*, 1916, 264.

[32] Beadle and Stevens, *Analyst*, 1911, **36**, 6–9; *J.*, 1911, 141.

[33] *Journ. Russ. Phys.-Chem. Soc.*, 1915, **47**, 1374-1441; *J.*, 1916, 57, 58.

[34] *Chem. Soc. Trans.*, 1915, **107**, 162–171; *J.*, 1915, 367.

[35] *Koll.-Zeits.*, 1914, **15**, 217–226; *J.*, 1915, 671.

[36] *Comptes rend.*, 1915, **161**, 589–591; *J.*, 1915, 1217.

[37] *Caoutchouc et Gutta Percha*, 1915, **12**, 8724–5; *J.*, 1915, 1104.

[38] *Rubber Industry*, 1914, 259–275; *J.*, 1915, 879.

[39] *Chem.-Zeit.*, 1914, **38**, 1249–1251; *J.*, 1915, 187.

[40] *Rubber Industry*, 1914, 205–211; *J.*, 1915, 725.

[41] *Ibid.*, 1914, 246–256; *J.*, 1915, 724.

[42] Various publications of Memmler and Schob, *Mitt. K. Materialprüfungsamt*, 1909, **4**, 173; 1911, **4**, 185; 1912, **3**, 140; 1913, **7** and **8**, 437.

[43] Beadle and Stevens, *Chem. News*, 1907, **96**, 37; *J.*, 1907, 935.

[44] *Rubber Industry*, 1914, 230–245.

[45] *Ibid.*, 1911, 371.

[46] *Ibid.*, 1914, 212–219; *J.*, 1915, 842.

[47] *Ibid.*, 1914, 284-293; *J.*, 1915, 880.

[48] *Ibid.*, 1914, 334, 335, and 337.

[49] *Journ. Russ. Phys.-Chem. Soc.*, 1915, 1453 *et seq.*; *J.*, 1916, 59.

[50] *Caoutchouc et Gutta Percha*, 1916, **13**, 8880.

[51] *Journ. Russ. Phys.-Chem. Soc.*, 1915, **47**, 1885 *et seq.*; *J.*, 1916, 369.

[52] *Ibid.*, 1915, **47**, 1904 *et seq.*; *J.*, 1916, 370.

[53] *Koll.-Zeits.*, **8**, 304; **9**, 300; **10**, 299; **11**, 28, 274; **13**, 265; *J.*, 1911, 816; 1912, 81, 651, 785; 1913, 97, 1120.

[54] *Journ. Russ. Phys.-Chem. Soc.*, 1915, **47**, 1459–60; *J.*, 1916, 59.

[55] Eng. Pat. 1894 (1915), *J.*, 1916, 479.

[56] *Rubber Industry*, 1914, 156–163; *J.*, 1915, 562. *Caoutchouc et Gutta Percha*, 1915, **12**, 8720–1; *J.*, 1915, 1105.

[57] *Caoutchouc et Gutta Percha*, 1910, **7**, 4371–4376; *J.*, 1910, 1169.

[58] *Rubber Industry*, 1914, 172–177; *J.*, 1915, 671.

[59] *Koll.-Zeits.*, Jan., 1914, **14**, 96.

[60] *India Rubber J.*, 1916, **51**, 661–2; *J.*, 1916, 643.

[61] *J.*, 1915, 524.

[62] Fr. Pat. 470883 (1913), *J.*, 1915, 188.

[63] Eng. Pat. 7370 (1914), *J.*, 1915, 436.

[64] Eng. Pat. 10833 (1914), *J.*, 1915, 436.

[65] Ger. Pat. 280198 (1914), *J.*, 1915, 436.

[66] *Journ. Russ. Phys.-Chem. Soc.*, 1915, **47**, 1892; *J.*, 1916, 370.

[67] *Gummi-Zeitung*, 1915, **29**, 424; *J.*, 1916, 643.

[68] *Journ. Russ. Phys.-Chem. Soc.*, 1915, **47**, 1441 *et seq.*, 1910 *et seq.*; *J.*, 1916, 58, 368.

[69] Fr. Pat. 475565, 1914; *J.*, 1916, 130.

[70] *Journ. Russ. Phys.-Chem. Soc.*, 1915, **47**, 1928–31; *J.*, 1916, 368.

[71] *Ber.*, 1914, **47**, 350–354; *J.*, 1914, 267.

[72] *Journ. Russ. Phys.-Chem. Soc.*, 1915, **47**, 1910; *J.*, 1916, 368.

[73] *Koll. Zeits.*, 1914, **15**, 126-131; *J.*, 1915, 500.
[74] *Annalen*, **406**, 173; *J.*, 1915, 670.
[75] Eng. Pat. 2070 (1914), *J.*, 1915, 238.
[76] Ger. Pat. 279780 (1914), *J.*, 1915, 436.
[77] Ger. Pat. 286640 (1913), *J.*, 1916, 431.
[78] Eng. Pat. 17253 (1914), *J.*, 1915, 915.
[79] Eng. Pat. 297 (1915), *J.*, 1915, 1217.
[80] *Journ. Russ. Phys.-Chem. Soc.*, 1915, **47**, 1472–1494 and 1947-1982; *J.*, 1916, 69, 380, 381.
[81] *Ibid.*, 1915, **47**, 1983–1988; *J.*, 1916, 381.
[82] *Ibid.*, 1915, **47**, 1494-1506; *J.*, 1916, 69.
[83] *Analyst*, 1913, **38**, 550; *J.*, 1914, 34.
[84] *J.*, 1915, 287.
[85] *Analyst*, 1915, **40**, 9–11; *J.*, 1915, 146.
[86] *Ann. Chim. Analyt.*, 1915, **20**, 214–6; *J.*, 1915, 1105.
[87] *U.S. Bureau of Standards, J. Franklin Inst.*, 1915, **179**, 353-4; *J.*, 1915, 436.
[88] *J. Ind. Eng. Chem.*, 1911, **3**, 734-7; *J.*, 1911, 1268.
[89] *Analyst*, 1915, **40**, 275–81; *J.*, 1915, 724.
[90] *J. Ind. Eng. Chem.*, 1916, **8**, 324–6; *J.*, 1916, 699.
[91] *U.S. Hygienic Laboratory*, Bull. No. 96, 55–62; *J.*, 1915, 40.

LEATHER AND GLUE.

By Joseph T. Wood.

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In the tanning industries, definite steps in advance, due to the application of science, are extremely difficult to detail on account of the secrecy in which individual manufacturers have shrouded their work. Even in the case of new materials, directly introduced as the result of chemical research, the methods of application are kept secret, and vary in each tannery. This policy is a legacy of the time not so far distant when every master tanner, and, indeed, almost every man in the yard, had his little budget of trade secrets.

Much of the work done during the past three years consists in the perfection of methods for exactly controlling the various tanning processes, and it is in this direction that the industry has benefited to the greatest extent. In all large works it is now the rule, rather than the exception, to find a chemist installed. The work of the International Association of Leather Trades' Chemists in Europe, and of the American Leather Chemists' Association in America, has been invaluable in standardizing methods of control.

In the analysis of tanning materials, although the method for the estimation of tannin is still an empirical one, namely, the measure of its absorption by hide, the technique is so worked out that the variation in the results of different chemists is now very small, whilst the tanner gets to know what he wants, namely, how much of the material will combine with hide. Until the chemistry of tannins is more completely known, we must be satisfied to use the hide powder method. A detailed account of this and other methods specially adapted to a tannery laboratory is given in *The Leather Chemists' Pocket Book* by Professor H. R. Procter and collaborators (Spon, 1912).

Preparatory Processes.

Preservation of Hides and Skins.—The question of the cause and prevention of salt stains has received much attention during the past few years. On the Continent the use of certain denaturing materials

has been found to cause salt stains. Abt[1] found that certain salt stains were caused by the presence of grains of calcium sulphate, which gave rise to a precipitate of calcium phosphate. In other stains, iron was an accessory cause. In others, again, he found bacteria which formed melanins. He recommends the addition of 4% of sodium carbonate to the salt as a denaturing agent.

In America, Yocum[2] investigated salt stains due to iron, originating from the blood. Lloyd[3] also contributes to the discussion. Becker[4] isolated several species of bacteria said to cause salt stains. In England the use of chemically pure salt[5] has been proposed and brought into use in some cases. For the preservation and disinfection of skins with special reference to anthrax, the process of A. Seymour Jones (formic acid and mercuric chloride) has been tried with some success. Much work has been done, especially in America, by Tilley,[6] who finds the Schattenfroh method (hydrochloric acid and salt) gives somewhat more constant results. (*See* also E. Moegle, *Centr. Bakt.*, **66**, 442; *Coll.*, 1913, 241.) A very useful account of the various problems which require dealing with in this section is contained in the Report of the International Commission on the Methods for the Preservation, Cure, and Disinfection of Hides and Skins, by A. Seymour Jones.[7] Mention should also be made of the important investigations into the ravages caused by the warblefly (*Hypoderma boris*), by Professor George H. Carpenter and Dr. T. R. Hewitt, of the Dept. of Agriculture and Technical Instruction for Ireland, published in the *Irish Naturalist*, October, 1914.

Soaking.—No great changes have taken place in this process, but it may be said that the advantage of assistants, such as small quantities of caustic soda and sodium sulphide, and of antiseptic methods generally, is fully recognized in all modern tanneries. A new process of soaking and softening hides and skins has been recently patented by Dr. Otto Röhm,[8] depending on the use of tryptic enzymes, but the process has not yet been introduced into general practice.

In the unhairing and bating process, the same chemist has proposed the use of proteolytic enzymes for removing hair or wool.[9] This

[1] *Bull. Soc. d'Encour.*, 1913, **119**, 646; *Coll.*, 1913, 204; *J.*, 1913, 616, 667.
[2] *J.A.L.C.A.*, 1913, **8**, 22; *J.*, 1913, 152.
[3] *Coll.*, 1913, 188; *J.*, 1913, 616.
[4] *Ibid.*, 1912, 408; *J.*, 1912, 829.
[5] A. Turnbull, *Leather Trades Year Book*, 1914, 181; *J.A.L.C.A.*, 1914, 412.
[6] *J.A.L.C.A.*, 1916, 131.
[7] *Coll.*, June, 1912 (Supplement).
[8] Ger. Pat. 288095, Nov. 12, 1914; *J.*, 1916, 372.
[9] Eng. Pat. 18870, 1911, *J.*, 1911, 1224.

process possesses advantages in the manufacture of chrome leather, but for vegetable tanned leather the fibres do not appear to be sufficiently split up. The process has been used in Germany and America, but so far has not been assimilated to English practice.

Liming, including Fellmongering.—Here again control of the whole of the processes has been the chief feature of the work done. Provisional methods of control were adoped at the London Conference of the I.A.L.T.C.[10] These methods have been also generally adopted by the A.L.C.A.

R. F. Innes[11] finds that in the preparation of lime-arsenic paints that the highest percentage of sulphur in combination with the lime is obtained by allowing the latter to be as fully hydrated as possible, and yet as hot as possible, before adding the arsenic. It should then be stirred very thoroughly.

In a recent paper by J. E. Pickles,[12] a working formula is given for a sulphur paint which may be used as a substitute for sodium sulphide. Half a pound of sulphur is boiled with excess of lime, and 33 oz. soda crystals added to the solution. This gives the same unhairing effect, and the same alkalinity, or causticity, as 3 lb. sodium sulphide crystals (Na_2S, $9H_2O$). When sulphur is boiled with milk of lime, a certain amount of calcium sulphydrate is formed, together with some polysulphides, the latter being rather advantageous than otherwise to the process. The sulphydrate has been shown to be the acting depilatory agent. By the omission of the soda an effect very similar to that of an arsenic lime is obtained.

The fellmongering of sheepskins in New South Wales is fully dealt with in a paper by F. A. Coombs, E. Swinbourne, and G. W. Gadd.[13]

A. A. Schlichte,[14] in a thesis presented to the University of Michigan, deals with the alterations in the structure of skin due to the liming process, in which he shows that, contrary to general belief, lime will unhair in sterile solution.

J. T. Wood and D. J. Law[15] show that both ammonia and sulphur compounds are formed from the hair of skins in sterile solutions, and that these products take part in the unhairing.

Rogers[16] contributes some useful notes on depilating, and D. McCandlish and J. A. Wilson[17] describe a reliable method for the

[10] *Coll.*, 1913, 73; 1914, 305.
[11] *J.*, 1914, 578.
[12] *J.*, 1916, 456.
[13] *J.*, 1916, 227.
[14] *J.A.L.C.A.*, 1915, 526; *J.*, 1915, 1218.
[15] *J.*, 1916, 585.
[16] *J.A.L.C.A.*, 1914, 42; *J.*, 1914, 152.
[17] *Ibid.*, 1913, 28; *J.*, 1913, 153.

determination of alkaline sulphides in the limes, based on Blockey and Mehd's method (*Coll.*, 1914, 75). The causes of error in the different methods of estimating sulphides in lime liquors have recently been discussed by H. G. Bennett (*Coll.*, Lond., 1916, 219).

An exhaustive résumé of the subject of unhairing and liming by W. Eitner was published in *Der Gerber* in 1913.[18]

Puering and Bating.—In the puering and bating processes the use of artificial bates has increased very considerably during the period under review. Most of these bates are based on the researches of Wood,[19] published in this Journal from 1894 onwards. The most successful of these bates is sold under the name of "Oropon."[20] This is composed of the enzyme of the pancreas absorbed in sawdust or kieselguhr, and then intimately mixed with varying proportions of ammonium chloride or boric acid, according to the kind of work for which it is destined to be used.

A similar preparation is in use in France under the name of "Confit Wood." These enzyme bates have been very successfully used for sheep and glove leathers, and also for split hides for boot uppers and glacé kid. There are some difficulties in the puering of hard goat skins, and also sheep grains for skivers, the difficulty with the latter being due to the prolonged liming the skins undergo. The prolonged action of lime so changes the chemical composition of the hyaline layer, and of the fibres immediately underlying it, that the former is capable of being attacked by tryptic enzymes, whereas the compound formed on or in the fibrous structure of the grain renders it more resistant to the action of the enzymes. The result is that in practice the hyaline layer of the skin is damaged before the remainder of the skin is sufficiently reduced or "down." There is little doubt that further research will overcome this difficulty.

Wood, in collaboration with H. J. S. Sand and D. J. Law, has investigated the action of the puering or bating process on the resiliency of the skin, using for this purpose the apparatus devised by Dr. Sand. By this means the degree of falling of the skins may be expressed numerically, and so recorded.[21]

The bacteriology of the bate has been further studied in America by William Cruess and Frank H. Wilson,[22] and John Helfrich contributes a valuable article on chemical control in the beam house.[23]

[18] *J.A.L.C.A.*, 1913, 482.

[19] *The Puering, Bating, and Drenching of Skins*, Spon, 1912; *Das Entkälken und Beizen von Fellen*, Vieweg, Braunschweig, 1914.

[20] See Eitner, *Der Gerber*, 1912, 311; *J.*, 1912, 1193.

[21] *J.*, 1913, 398.

[22] *J.A.L.C.A.*, 1913, **8**, 180; *J.*, 1913, 617.

[23] *Ibid.*, 1915, 396.

The following references to deliming, puering and bating processes may be mentioned :—

"The Acid Deliming Process," H. R. Procter, *Tanners' Year Book*, 1913, 75.

"Process for Bating Skins," Eberle and Co., Stuttgart. Eng. Pat. 22753, Nov. 19, 1914; *J.*, 1916, 430. See also Eng. Pat. 21202 of 1909; *J.*, 1910, 226.

"Improvements in the Preparation of Skins for Tanning," S. W. Cook, Eng. Pat. 24418, Dec. 21, 1914; *J.*, 1915, 1218.

"Process for Puering Skins," L. Krall, Fr. Pat. 469758, Mar. 18, 1914; *J.*, 1915, 42.

"Analysis of Material used in Beam House Procedure," C. R. Oberfell, *J.A.L.C.A.*, 1915, 252.

"Process for Deliming and Bating Hides and Skins," P. Schneider, *D.R.P.* 268236. In this process acid salts, such as sodium bisulphate, together with boric acid and sugar, are used. The process is more of a deliming than a puering process.

Pickling.—This process has come into increasing use year by year, not only as a preservative treatment, but more especially as a preliminary treatment in the manufacture of a great variety of leathers, principally chrome tanned, *e.g.*, split hides for boot uppers, sheep leather for gloving and for motor clothing, etc. No new methods have been adopted, but a great deal of light has been thrown on the theory of the process by the work of Procter and his pupils.

In the following references, the process is described and briefly discussed in 1 and 2. In 3 and 6 the control of the process in the works is described, and in 4, 5, and 7, the physical and chemical actions involved are fully discussed :—

1. "The Rising or Pickling of Skins," J. T. Wood, *Tanners' Year Book*, 1912, 115.
2. "Note on the Pickling Process," Professor H. R. Procter, *J.A.L.C.A.*, 1913, 7.
3. "Chemical Data from the Pickle Solution," P. M. Randall, *J.A.L.C.A.*, 1915, 171.
4. "The Equilibrium of Dilute Hydrochloric Acid and Gelatin," H. R. Procter, *Chem. Soc. Trans.*, 1914, 313; *J.*, 1914, 326.
5. "The Acid Gelatin Equilibrium," H. R. Procter and J. A. Wilson, *Chem. Soc. Trans.*, 1916, 307; *J.*, 1916, 645.

6. "Fellmongering and Tanning Sheepskins in New South Wales." F. A. Coombs, E. Swinbourne, and G. W. Gabb, *J.*, 1916, 227.
7. "Swelling of Gelatinous Tissues," H. R. Procter and D. Burton. *J.*, 1916, 404. Discussion, *J.*, 1916, 675.

Tanning Processes.

(a) *Vegetable Tannage.*—This is still the most important tanning process.

Neradol.—The most striking advance in this section is the commercial production of a synthetic tannin due to E. Stiasny.[24] Neradol[25] is prepared by the action of formaldehyde upon phenolic bodies under such conditions that only water-soluble products are obtained. The original material was put on the market by the Badische Anilin und Soda Fabrik, but since the War, several English firms have begun to manufacture it with success. Their products are sold under the names of: Synthetic Tannin, Paradol, Cresyntan, and Syntan.

Used alone, neradol gives a white-coloured, rather empty leather. The material strikes through the skin very rapidly, and it may thus be used as a preliminary tannage to shorten the time occupied in passing the goods through weak liquors; they can then be transferred direct to strong liquors of the usual vegetable tanning materials without danger of drawn grain or "case hardening." Great advances in our knowledge of the vegetable tanning process may be expected from the introduction of such materials, since the constitution of such synthetic tannins can be varied or modified in a controllable way; then the connection between constitution and tanning effects can be studied, and the question be answered how far the differences in the tannin molecule are responsible for differences in the leather produced.

References.—H. Dierdorf, *Coll.*, 1913, 366; Grasser, *Coll.*, 1913, 413; Eitner, *Der Gerber*, **39**, No. 931; Moeller, *Coll.*, 1913, 487, 593; Stiasny, *Coll.*, 1913, 528, 597 (a reply).

J. L. Van Gijn and H. Van der Waerden, in Holland, have investigated the pentose content of various tannin materials, and described the method for the estimation of pentoses by precipitation of furfurol with phloroglucin. The method is useful in detecting the presence of quebracho extract and chestnut extract and also for the estimation of lignin.[26]

Electric Tanning.—The use of an electric current to aid tanning has

[24] *Coll.*, 1913, 142; *J.*, 1913, 775.
[25] Ger. Pat. 262558, Sept. 12, 1911, *J.*, 1913, 878.
[26] *Coll.*, 1913, 639; *J.*, 1914, 151.

been further investigated by O. J. Williams[27] and K. Rideal and U. R. Evans.[28] The conclusions drawn are that the direct current destroys the tan in a tan liquor, but that an alternating current has not this destructive effect, and may accelerate the tannage by cataphoresis.

(b) *Mineral Tannages.*—The principal tannage in this class is by means of chrome salts. It has not only held its place, but largely displaced vegetable tannages for upper leather, and it is also coming into considerable use for sole leather. For the latter much ingenuity and long trials have at last overcome the difficulties due to the stretching of the leather and to its slippiness in use. Chrome tanning generally is very fully treated in the *Handbuch der Chromgerbung* by Joseph Jettmar (Schulze und Co., Leipzig, 1913).

R. F. Innes[29] has shown that the chrome content of a given leather gives no information as to possible causes of harshness, tinniness, or break, whereas a microscopic examination of the fibres often gives very useful information. The paper is illustrated by photographs of the fibres of chrome tanned glacé goat.

Procter and Wilson,[30] from an investigation as to the causes of undertanning with certain one-bath liquors, find this to be due to salts of hydroxyacids, which, when present in sufficient quantity, entirely prevent the tanning. They further show that chrome tanning, unlike vegetable tanning, is a reversible process.

Procter has made several practical suggestions arising from a consideration of the research. One of these was that hides, or kips, could be partially chromed, and in that state can be split more readily than in the lime. The grain can be tanned out in chrome liquors, and the flesh split, which is best tanned in vegetable liquors, can be stripped of all chrome by means of a solution of Rochelle salt, or other salt of a hydroxyacid, and afterwards tanned in any way desired. A further use of the idea is that chrome pieces and shavings may be stripped of chrome and used in the manufacture of glue and gelatin.

Several other processes have been proposed for dechroming chrome-tanned leather for the preparation of glue. S. R. Trotman[31] treats the leather with sodium peroxide. Oxidation of the chrome to sodium chromate takes place. This is removed from the leather by washing and then recovered. W. Prager[32] uses 2 per cent. sodium bisulphate at 45° C., whereby the basic chrome salt in the leather is changed into the

[27] *Collr.*, 1913, 76; *J.*, 1913, 373.
[28] *J.*, 1913, 633.
[29] *J.*, 1914, 579.
[30] *J.*, 1916, 156.
[31] Eng. Pats. 5676, Mar. 7, and 12393, May 23, 1911, *J.*, 1911, 1462.
[32] D.R.-P. 257286, June 15, 1912, *J.*, 1913, 501.

normal soluble salt. The latter is then washed away, and the leather finally neutralized with lime.

So far as my knowledge goes, there have been no changes in the alum tanning process, though here it seems possible to effect improvements by utilizing basic aluminium salts somewhat after the methods of one-bath chrome tanning. This was originally proposed by Bertram Hunt.[33]

(c) *Oil and Aldehyde Tannages.*—Oil leather dressing or chamoising has not undergone any change during the period under review, but Lewkowitsch and Wood[34] have shown that the use of neutral fish oils is not essential for the tannage, but that the free fatty acids can tan even quicker than the neutral oils, or glycerides. The process has not been successful commercially owing to the by-products—*e.g.*, sod oil—being of a different character from that produced from the original oils. The discovery, however, throws a good deal of light on the chemistry of the oil leather tannage.

Tannage by means of formaldehyde, invented by Payne and Pullman in 1898,[35] has been improved and come into increasing use in the manufacture of white washable gloving leather. The skins used are mostly lamb splits or "linings." The leather is perfectly white, and improves by washing. The manipulation of the skins and details of the process are, more or less, kept secret.

Finishing Processes.

These are of almost infinite variety, including not only ordinary finishing of sole leather and dressing hides for the market and of upper leather in blacks or colours, but all kinds of fancy leathers, buffed, printed or velvet finish for bags, bookbinding, and leather goods generally. As a rule, the leather, especially sheep-skins, is degreased before dyeing and finishing, although in recent practice it is frequently dyed before degreasing. Modern degreasing plants owe their origin to F. N. Turney.[36] The solvent used is generally petrol spirit or benzene, which is completely recovered by distillation. Other degreasing plants on a slightly different principle have been constructed by W. J. Sagar.[37]

[33] Eng. Pat. 15607, 1884, *J.*, 1885, 747.

[34] Eng. Pat. 13126, 1911, *J.*, 1912, 597.

[35] Eng. Pat. 2872, 1898, *J.*, 1899, 504. See also Meunier, *Coll.*, 1912, 420.

[36] Eng. Pats. 8179 of 1893, 14978 of 1895, 1370 and 18360 of 1896, *J.*, 1894, 633; 1896, 589; 1897, 41, 677.

[37] Eng. Pat. 13778 of 1897, *J.*, 1897, 816.

Recently other solvents, which have the advantage of being non-inflammable, have been tried, the most promising being trichlorethylene (C_2HCl_3), sold under the name of Westrosol. It may be used in the dry way the same as benzene, but it has also been applied in admixture with soap to wet skins. The wet process has not come into general use in England, as it cannot compete with the dry process.[38] It may be noted that trichlorethylene has a toxic effect, and it is very probable that this would cause trouble if it came into general use.

Oskar Trebitsch has patented[39] the use of peptone and similar hydrolyzed albumins for the fixation of tannin in sole leather and also for fixing the colours on dyed leather. Such products are stated to act better than albumin, which is generally used, since they have no hardening effect, but, on the contrary, make the leather softer.

J. T. Donald[40] contributes a useful paper on modern shoe polishes and dressing, in which the compositions required for various kinds of leather are dealt with.

In the older process of japanning with linseed oil the leather requires exposure to sunlight in order to toughen the varnish. It has been found that this effect is due to the action of the ultra-violet rays in the sunlight. As is well known, ultra-violet rays are absorbed by glass, but pass freely through quartz. A large plant for the treatment of enamel leather by ultra-violet light from mercury quartz lamps is at present installed in a German leather works. The effect is said to be exactly similar to that of sunlight, and consequently, because of that, the manufacturer is independent of the weather. (*See* Eng. Pat. 10971, 1912, *J.*, 1912, 694 ; U.S. Pat. 1,099,378, 1910 : also supplementary Fr. Pat. 443406, 1913, *Coll.*, 1913, 337.)

Collodion or nitrocellulose dissolved in amyl acetate and other solvents, alone or in mixture with oil products, has largely taken the place of linseed oil in japanning. The advantage of the process over the older method is that no ovens are required, exposure to sunlight is not necessary, and the leather retains its natural grained surface, which is visible through the transparent coating. The enamel has not the same tendency to crack as the linseed oil varnish.

Doerr and Reinhardt[41] have patented the use of ammonia vapour in the final drying of japanned leather. The vapour is produced by exposing ammonia solution, sp. gr. 0·950 to 0·960, in the drying-stove during the final drying-off process.

Fat Liquors.—The use of emulsions of oils in water and soap solutions

[38] *Coll.*, 1913, 61.
[39] D.R.-P. 265913, *J.*, 1913, 1121.
[40] *J.*, 1913, 459.
[41] D.R.-P. 267524, *Coll.*, 1914, 41.

is an integral part of the chrome tanning process where the leather must be dyed and fat liquored before being dried out. Fat liquors are also applied to vegetable tannages both before dyeing and also in the dye bath. The scientific aspect of these emulsions has already been developed by Meunier.[42]

The principal change has been in the increased use of sulphonated oils (sulphonated castor oil and sulphonated cod oil). These oils are now added to the dye bath, and are also used in the preparation of soft leathers, such as the jerkin basils for the lining of soldiers' winter clothing. They have the valuable property of emulsifying larger quantities of neutral and even of mineral oils. The increased use of these oils has necessitated new methods of analysis for their commercial valuation. Combined SO_3, total neutral oil, and moisture are the figures usually required. The method of analysis prescribed by the A.L.C.A.[43] is quite satisfactory for general control work. Other papers which may be consulted are as follows:—

"Développement de l'emploi des huiles emulsionnables, et des emulsions en tanneries," U. J. Thuau, *Coll.*, 1913, 219 and 335; *J.*, 1913, 617.

"The Constants of the Fatty Acids from Sulphonated Cod Oil," L. G. Radcliffe and C. W. Palmer, *J.*, 1915, 643.

"Sulphonated Cod Oils," Dr. G. Bumcke, *J.A.L.C.A.*, 1915, 559; *J.*, 1915, 1214 (an excellent discussion of the various methods of analysis).

"Analysis of Turkey Red Oil," M. Herbig, *Les Matières Grasses*, 1915, 4316; *J.A.L.C.A.*, 1915, 437.

"Notes on Sulphonated Oil Analysis," W. K. Alsop and L. A. Cuthbert, *J.A.L.C.A.*, 1916, 364 (an interesting discussion on the constitution and analysis of sulphonated oils).

Waste Products.—The economical disposal of tannery waste has not received the attention in this country that it has in America. Meunier[44] recommends that the various effluents from the tanneries should be mixed together for settlement; the combination of tannin and lime, chrome, and dye liquors, when blended together, forms heavy and easily separable sediments. He also gives analyses of the various waste liquors from a sole leather tannery, using vegetable tanning materials only.

[42] *Coll.*, 1910, 222, 277; *J.*, 1910, 102.
[43] *J.A.L.C.A.*, 1914, 68; *J.*, 1914, 266.
[44] *Coll.*, 1912, 268.

F. P. Veitch[45] gives particulars of sewage disposal plant at Gloversville, New York, where there are a large number of tanneries, and where the purification of the waste is largely a problem of the purification of the tannery effluent. In a further paper[46] the same author states that the amount of effluent from tanneries varies from 100 to 375 gallons effluent per day per hide. The following figures on the character and distribution of the effluent from a tannery, handling about 3000 horse and calf hides per day, are of interest: 4000 gallons of spent soak, 1200 gallons of spent chrome liquor, 1200 gallons of spent pickle, 1000 gallons of spent bate, 7650 gallons of sulphide sludge, 121,500 gallons of wash water, making a total of 136,550 gallons, of which about 15,000 gallons are what may be termed highly impure wastes, the remainder being water wash, which, from the nature of its use, can contain but little dissolved matter.

Sedimentation is absolutely necessary. The sewage on entering the filter should contain less than 300 parts per million of suspended matter. The lime mud from the unhairing pits should be kept separate from the other waste, and only the liquid portion mixed with the other waste liquors. It may be remarked that this is contrary to the usual recommendation, but it has been found that if the lime mud is mixed with the effluent, the volume of sludge is greatly increased, and its fertilizer value materially reduced, because so large a quantity of inert material is mixed with the nitrogenous matter, the most valuable constituent of the settled sludge. The lime mud should always be kept separate from the other waste, and sold or given away by itself.

Treatment of the effluent from the filters with hypochlorite at the rate of 5 to 10 parts chlorine per million, will make the material comply with all reasonable requirements as to purity. The total cost of purification plants, depending on construction and local conditions, may vary from about $35,000 to $75,000 for 1,000,000 gallons per 24 hours. Tables are given showing area, cost, and capacity of work for treating this quantity of sewage.

A. Roth[47] gives an account of the results obtained by the Massachusetts State Board of Health, in which it is stated that a bacteriological treatment of the wastes is possible, and that several plants are in operation. The preliminary treatment is a settling process, which is allowed to take place in a continuous flow tank of sufficient size, the length and breadth being so proportioned that the

[45] *J.A.L.C.A.*, 1913, 10; *J.*, 1913, 153.
[46] *Ibid.*, 1915, 126; *J.*, 1915, 437.
[47] *Ibid.*, 1914, 512; *J.*, 1915, 41.

velocity of the sewage shall at no point be sufficient to disturb the settling action. In the Michigan Tannery and Extract Company's plant at Fremont (Mich.), working 300 hides per day, with a total waste water flow of 400,000 gallons per 24 hours, seven sedimentation tanks, 13 × 50 ft. and 55 in. deep, are used. In addition there are two small continuous upward-flow sand beds, with an area of 500 sq. ft. each. Alumino-ferric is used as a coagulant to aid in the sedimentation, and to discharge the colour. No attempt is made to obtain a stable non-putrescible effluent by filtration, as the effluent from the continuous upward-flow sand bed is discharged directly into the creek.

The problem of dealing with the sludge is difficult, special drying devices, sludge presses, etc., being required unless large space is available for natural drying. Even after sedimentation, the wastes contain more dissolved organic matter than is present in ordinary domestic sewage. Further treatment of the waste is therefore imperative. Some form of filtration is necessary, as sewage farming requires too much land. Intermittent sand filtration has proved satisfactory if sufficient time is allowed for the aeration of the bed. The degree of purification depends on the condition of the bacteriological film and the supply of oxygen. The cost of treatment in the above-mentioned plant, for operation only, was about £1,000 per annum.

C. C. Smoot[48] gives analyses of partially dried sludge, and of the effluent from an American sole leather tannery. The solid matter was analysed by the State Department of Agriculture, and found to be particularly adapted for the manuring of fruit trees.

J. W. Phelan and J. H. Cohen[49] give details of a rapid filter system (Moore Slime Filter) to handle one million gallons of effluent per day.

With regard to the attempts to produce a satisfactory effluent by the so-called "activated sludge process," important general papers by E. Ardern and W. T. Lockett[50] may be consulted.

Machinery.

Generally speaking, there has been a great change in the attitude of manufacturers towards the use of machinery, especially during the last three years, and great strides have been made in the use of machinery for all branches of the leather industries.

One of the chief advances has been in the introduction of the pneumatic roller fleshing machine, by the Turner Tanning Machine

[48] *J.A.L.C.A.*, 1914, 523; *J.*, 1915, 41.
[49] *Ibid.*, 1913, 426; *J.*, 1913, 1024.
[50] *J.*, 1914, 523; 1915, 937.

Company, of Peabody, Mass. The machine is constructed in a similar way to the modern type of fleshing machine, but instead of a solid rubber roller, there is a flexible hollow bed roller, connected with a pressure tank gauge, an automatic relief valve, and a constantly running pump. There is thus an open flow of air in and out of the bed, and the support is constantly and instantly varying in quantity as the width and thickness of the hide changes. The pressure of air on the support may be altered when desired without stopping the machine. By means of this improvement, the bellies and shanks are fleshed as clean as the backs, and the loss of weight by too clean fleshing of the heavy parts is avoided.

Another machine which has been largely introduced in America, also by the Turner Machine Company, is a power hydraulic press, in which the leather is placed on a table, and a platen brought down upon it with a pressure of about 75 tons. The result is a greatly improved feel of the leather—the elimination of growth wrinkles, and greatly increased cutting value.

The machine is also used for chrome sole leather, and can be used on cut pieces of other heavy leathers to good advantage.

A striking-out machine is now made in this country capable of setting out the very thinnest skins, such as skivers, quite as well as thicker skins.

Blacking and seasoning machines have also come largely into use. Several new measuring machines, based on the principle of the old Sawyer machine, have been put upon the market, which are very reliable.

The National Physical Laboratory now standardize templates for checking the results of these machines, and after the War the whole question of the measurement of leather will be placed under the Weights and Measures Act.

Chemistry and Analytical Methods.

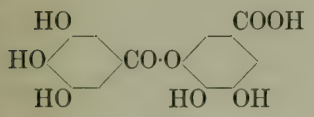
Some of the chemical problems involved have already been referred to, since it is not possible to separate the chemistry of the various processes from the practical work of leather making. The chemistry of the tannins has been the subject of continuous research.

Nierenstein and various collaborators at Bristol have continued to examine tannins and other products, such as ellagic acid[51] and catechins,[52] with a view of determining their chemical constitution.

[51] Nierenstein and Rixon, *Coll.*, 1913, 53.
[52] Nierenstein, *Coll.*, 1913, 200.

Nierenstein considers tannin, or gallotannic acid, to consist of a mixture of digallic acid (I) and leuco-tannin (II).

I.



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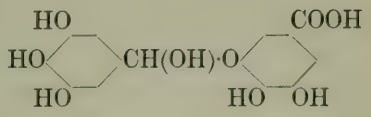
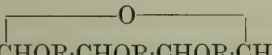


Emil Fischer,[53] after purifying gallotannic acid by solution in aqueous alkali, and extraction with ethyl acetate, as had been done by Stiasny and Paniker,[54] so that it contained no free carboxyl group, found it to yield on hydrolysis with sulphuric acid 7 to 8 per cent. of glucose, the other product being gallic acid. The conclusion drawn was that one molecule of glucose was combined with ten molecules of gallic acid.

In a further paper Fischer and Freudenberg described an attempt to synthesize gallotannic acid by starting with the methylo-tannin of Herzig and his pupils. They obtained in this way a body which is shown to be pentadigalloyl-glucose, and which, if not identical with tannin, is so nearly related to it that the synthesis may be said to be accomplished. The structure of the tannin molecule may therefore be represented thus :



$$\text{CHOR·CHOR·CHOR·CH·CHOR·CH}_2\text{OR},$$

where R = $(HO)_3C_6H_2\cdot CO\cdot O\cdot C_6H_2(OH)_2CO$.

For an account of this work, see *Berichte*, **46** (1913), 3253, *Coll.*, 1914, 8. Fischer does not think his products can be of any use to the practical tanner, who can only consider much cheaper materials, such as Neradol.[55]

A large number of papers on analytical methods have been published, chiefly in connection with the estimation of tannin, but, as stated in the introduction, the hide powder method as specified by the I.A.L.T.C. and the A.L.C.A. still holds the field.

[53] *Coll.*, 1914, 8. [54] *Chem. Soc. Trans.*, 1911, **99**, 1819.

[55] Mr. F. C. Thompson points out that Fischer's attempt to synthesize gallotannic acid was by the condensation of glucose and the acid chloride of digallic acid, and the success of this attempt, according to Fischer himself, was not certain. He considers the preparation of gallotannic acid from methylotannin next to an impossibility. The methoxy groups could only be removed by the action of hydriodic acid, a procedure far too drastic for the stability of the gallotannic acid molecule.

The attraction of a definite chemical method for the estimation of tannin still claims the attention of chemists, especially the use of copper and nickel salts. It may be pointed out that such precipitation methods are quite as empirical and unsatisfactory as the hide powder method, since in both cases we have to deal with colloidal precipitation, and the composition of the compound formed depends upon a number of physical relations, which it is extremely difficult to keep constant.

The following list of papers and notes will be sufficient to give an idea of the work done in connection with the analysis of tanning materials:—

H. G. Bennett, "Analysis of Tanning Materials," *J.*, 1914, 1182; 1915, 473 and 822. "Note on the Tannins of Valonia, Oakwood, and Chestnut Wood," *J.*, 1914, 1186.

A. T. Hough, "Notes on the Application of Tungsten Salts to the Analysis of Tanning Materials," *J.*, 1914, 847.

Puran Singh, "Nickel Tannates," *J.*, 1914, 172.

D. B. Dott, "Note on the Determination of Tannin," *J.*, 1915, 1124.

A. T. Hough, "Analysis of Tanning Materials," *J.*, 1915, 472.

F. A. Coombs and A. H. Dettmann, "Notes on Australian Pine Barks," *J.*, 1914, 232.

T. Callan, "Note on the Analysis of Guara and Guara Extract," *J.*, 1915, 645.

T. Callan, "Note on the Analysis of Tanning Materials," *J.*, 1915, 646.

Puran Singh, "Note on the Addition of Fat to Tannin Extracts," *J.*, 1915, 208.

Puran Singh and T. F. Ghose, "The Use of Nickel Hydroxide in Tannin Estimation," *J.*, 1916, 159.

The analysis of sole leather is dealt with very comprehensively by F. P. Veitch and J. S. Rogers,[56] and that of East India leathers by M. C. Lamb.[57]

Some Effects of the War on the Tanning Industry in General.

The great change that has taken place has been the cutting off, by reason of the War, of our supplies of oak wood extract, which comes from Hungary, the import of valonia from Smyrna, and, finally, labour

[56] *J.A.L.C.A.*, 1913, 286.
[57] *Coll.* (London), 1915, 111.

difficulties. Practically no French extract came over for a long time. Our tanners had therefore to draw increased quantities of mimosa bark from South Africa, myrabolams from India, gambier from Singapore, and quebracho extract from the Argentine. Supplies of chestnut extract were also obtained from the United States, and, although the quality is inferior to the French extract, it helped to keep the tanneries going. British extract manufacturers increased their plant, and came to the assistance of tanners by making a blended extract with quebracho and myrabolams. They also made an extract from mimosa bark, and the latter is now being made in South Africa. We are also getting myrabolam extract from India.

The probable result of all this has been that the British tanner has used more fibre in the tanning of his leather—in fact, has gone back to the process adopted 20 or 30 years ago, before extract was so plentiful and cheap. This has not improved the colour of the sole leather, but probably the quality has been, if anything, better than it was prior to the War, because we have lacked the bleaching agents that tanners were using.

We have also been handicapped considerably by the price of such materials as lactic, formic, and oxalic acids. The two former are used for deliming, and oxalic acid is used to a certain extent in the early liquors to throw out lime salts and improve the colour of the leather.

Glue Manufacture.

During the last three years there have been no striking advances in the methods of manufacture, but there has certainly been an awakening to the value of scientific control of the processes, and the control of raw and finished products. This has been largely rendered necessary by the difficulty of the bone market and the competition of the German combine. There has been an increasing tendency to concentrate on one product, and to pay more attention to by-products.

Owing to the increasing demand for gelatin, many who formerly only made glue are now producing this substance. This in itself has made it necessary to be much more careful about the details of manufacture, and thus indirectly the quality of the glue has also improved.

Many patent processes have been brought out, but none appears to be commercially successful. There is still a marked disinclination on the part of manufacturers to spend money on experiments.

Among the patents taken out is a process for treating bones with a solution of peroxide or percarbonate of sodium.[58] It is said to

[58] H. Benzel, Fr. Pat. 460611, *J.*, 1914, 95; Eng. Pat. 24135, 1913, *J.*, 1914, 759.

be much quicker than the usual treatment of lime, and a better coloured product is obtained. While this process is too costly for ordinary glue, it is said to be effective in the manufacture of gelatin. Trotman's process for preparing glue from chrome leather pieces has already been mentioned, p. 232.

The testing of glue has received a good deal of attention during the last few years, and specifications for checking the quality of cabinet glue have been drawn up by the American Society for Testing Materials.[59]

There is also some interesting information on the chemistry and quantitative determination of gelatin by M. Berrar.[60]

[59] *J.*, 1914, 1021. See also "A Study of Various Tests upon Glue, particularly the Tensile Strength," A. H. Gill, *J. Ind. Eng. Chem.*, 1915, **7**, 102; *J.*, 1915, 292.

[60] *Biochem. Zeits.*, 1912, **47**, 189–214; *J.*, 1913, 37.

FERMENTATION INDUSTRIES.

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Introductory.

In presenting this Report on the progress which has been achieved in researches connected with the Fermentation Industries from the period of January, 1914, to June, 1916, the writer wishes to point out that whilst he does not claim that it is exhaustive, he has endeavoured to collate researches which on the one hand show some novelty and suggest future lines of research, and on the other hand those which appear to him to mark a definite issue.

Scientific work in connection with the Fermentation Industries covers a large number of subjects, and the writer has deemed it advisable to arrange the matters dealt with in sections.

Unquestionably a great event in the period covered by this Report is the publication of Dr. H. T. Brown's "Reminiscences of Fifty Years' Experience of the Application of Scientific Method to Brewing Practice."[1] Dr. Brown gives a retrospect of fifty years' work, and points out that the advances in our knowledge which were the outcome of studies on fermentation, reach far beyond the aims for which they were carried out. In his opening remarks he states :—

> "Looked at from the point of view of the far-reaching nature of its principles, brewing is an industry which is capable of yielding in kind a very high rate of interest on the scientific knowledge sunk in it."

Those who study this most able retrospect will find the author's words are fully justified.

Indeed, to mention but one instance, Pasteur's "Etudes sur la Bière" are well known to have been the forerunner of Lister's work on antiseptic and subsequently aseptic surgery. The late Prof. Marshall Ward once remarked that he had come to the conclusion that brewers

[1] *J. Inst. Brewing*, 1916, **22**, 265.

were in a sense agriculturists, and viewed in this light, fermentation research may be said to have thrown a flood of light on agricultural questions. Inasmuch as generations of micro-organisms succeed one another with such rapidity, a zymologist, from his work, obtains an answer, and a much more precise one, to problems in metabolism in as many days as does the agriculturist in years, and the answer is usually suggestive to the agriculturist.

Chemistry.

Starch.—The number of papers dealing with starch and its products of hydrolysis has exhibited a falling off during recent years, it having apparently been recognized that the practical value of such work, although important, has been exaggerated. So far as raw grain conversion, carried out with a minimal quantity of malt such as in distillery mashes for the manufacture of so-called grain spirit, is concerned, researches on starch hydrolysis are directly applicable. But even then each particular grist must be studied under the conditions which obtain in practice. In the brewers' mash-tun, on the other hand, it is not a question of production of alcohol alone but of flavour, fulness and many other qualities. Here we are dealing principally with a malt mash, and malt, it must be remembered, contains many other substances, both actually and potentially soluble, besides starch conversion products. It is certain that combinations of carbohydrates containing an open carbonyl with amino-acids occur at mashing temperatures (cp. Malting, p. 254). If that be so, the study of starch hydrolysis *per se* only affords at most a partial explanation of the brewers' mash-tun conversions.

The repeated observations of the writer during the past twenty years, that dextrose is among the products of the prolonged action of malt diastase on starch, have received ample confirmation from many workers on the subject. It is somewhat surprising, therefore, to find that O. v. Friedrichs[2] suggests a configuration for starch which provides for its complete conversion into maltose by malt diastase. As long ago as 1902, B. F. Davis and the writer pointed out[3] that potato starch paste was readily hydrolysed by malt diastase to a point where the dissolved solids had the constants of maltose, but it is very difficult to isolate maltose from such a solution, which subsequent experiments have shown to contain other carbohydrates, and apparently i.a. Syniewski's dextrinose (isomaltose). Bearing on this point, J. L. Baker and H. F. E.

[2] *Archiv for Kemi. Mineral. Och. Geologi*, 1913, **5**, 37.
[3] *J. Inst. Brewin* 1902, **8**, 482; *J.*, 1902, **21**, 1088.

Hulton[4] find that, contrary to H. T. Brown's and G. H. Morris's statement[5] that maltose is the sole product of the action of malt diastase on barley starch granules, the products are dextrins, maltose, dextrose, and a dextrin-like carbohydrate of the same molecular weight as maltose. O. v. Friedrichs (*loc. cit.*) has studied the action of oxalic acid on starch, and finds the products to consist of maltodextrins (including two probably identical with the maltodextrins-α and -β of Ling and Baker), maltose, dextrose and a glucosid-β dextrose (isomaltose) which forms a phenylosazone malting at 146° C.

By the action of concentrated hydrochloric acid on dextrose at 10° C. for 24 hours, v. Friedrichs[6] states that he obtained dextrose (18 %), isomaltose (18 %), maltose (8 %), and an unknown polysaccharide (6 %).

The work of W. A. Davis and his colleagues on the formation and translocation of carbohydrates in plants[7] is of the highest importance to the plant physiologist, and the same may be said of other papers by the same anthors[8] on the distribution of maltase in plants. The writer is unable to agree with these authors that the dextrose found by him in commercial concentrated malt extracts owed its origin to the action of maltase on maltose.

Proteins and their derivatives.—C. Neuberg[9] extracted 82 grams of coagulable protein from the maceration juice obtained from 500 grams of dried yeast. He estimated the phosphorus content of the product, and concluded that it comprised 3 % of nucleo-protein. He has demonstrated the presence of alanine and tryptophane in the juice besides other bases. J. Meisenheimer[10] has investigated the mono-amino acids of yeast autolyzed in presence of toluene. For this purpose he used E. Fischer's esterification method. He identified glycine, alanine, valine, leucine, proline, phenylalanine, aspartic and glutamic acids, tyrosine, and tryptophane.

Diastase.—F. Emslander has carried out a long series of experiments on the significance of the concentration of hydrogen ions on the brewing process,[11] and he points out that a better insight would be secured if the question of acidity were regarded from the point of view of hydrogen ion concentration rather than that of "titration" acidity.

[4] *J. Chem. Soc. Trans.*, 1914, **105**, 1529; *J.*, 1914, **33**, 760.
[5] *Ibid.*, 1890, **57**, 510; 1901, **79**, 1085. [6] *Ibid.*, **4**, 1.
[7] *J. Agric. Science*, 1916, **7**, 255, 327, 352; *J.*, 1916, **35**, 373, 374.
[8] *Bio-chemical J.*, 1916, **10**, 31, 49, 56.
[9] *Woch. für Brau.*, 1915, **32**, 317.
[10] *Ibid.*, 1915, **32**, 325.
[11] *Zeits. ges. Brauw.*, 1914, **37**, 2, 16, 27, 37; *J.*, 1914, **33**, 212.

In a further paper[12] he states that the concentration of hydrogen ions in beer never exceeds $H^{-4\cdot4}$, neutrality being $H^{-7\cdot07}$. He advises determining the acidity electrometrically before and after adding a known volume of N/10 alkali.

H. C. Sherman and A. W. Thomas[13] show that weak and strong acids and phosphates exhibit their maximum stimulating action on malt diastase at a concentration of hydrogen ions between $P_H = 4\cdot2$ and 4·6, corresponding approximately with 0·0006 N acetic acid or 0·0002 N hydrochloric acid. This is Sörensen's exponent, and is equivalent to $H^{\cdot} = 10^{-4\cdot2}$ and $H^{\cdot} = 10^{-4\cdot6}$.

J. Takamine[14] has published an interesting paper on the preparation of taka-diastase from the products of the action of *Aspergillus oryzæ* on wheat bran. He states that the product contains, besides amylase, invertase, maltase, cytase, oxidase, lipase, peptase, and ereptase. A. Compton[15] finds that in the hydrolysis of salicin by emulsin, or of maltose by taka-diastase, the optimum temperature is independent of the concentration of substrate and of enzyme. It varies, however, considerably with the concentration of hydrogen ions. If the latter be $10^{-7\cdot2}$ in the case of taka-diastase, the optimum temperature is 49° C., or if 10^{-3} the optimum temperature falls to 35·5° C.

Continuing his most remarkable observations on the "activating" of carbohydrates, T. Panzer[16] states that if dry lactose be treated with dry hydrogen chloride and subsequently with ammonia, it acquires feeble amylolytic power. The same, he states, is true of starches, dextrins, gum arabic, maltose, dextrose, lævulose, and galactose.

Proteolytic Enzymes.—H. Schjerning,[17] in a very comprehensive paper on the transformation of the proteins of barley during malting, shows that if these changes have not been carried far enough in the malt-house, the fault cannot be rectified by modulating the mashing process, and thereby making use of the proteolytic enzymes of malt.

E. Westergaard[18] shows that the proteolytic activity of malt increases fairly rapidly up to about 50° C., then more slowly to 58° C., after which it falls off. The optimum temperature for the action of malt extract on peptone (in which case, he states, two enzymes are concerned) appears to lie between 25° and 37° C. Brewers' yeast was

[12] *Zeits. ges. Brauw.*, **37**, 164.
[13] *J. Amer. Chem. Soc.*, 1915, **37**, 625; *J.*, 1915, **34**, 371.
[14] *Chem. News*, 1914, **110**, 215; *J.*, 1914, **33**, 1068.
[15] *Proc. Roy. Soc.*, 1914, **87B**, 245; **88B**, 258; 1915, **88B**, 408; *J.*, 1914, **33**, 977; 1915, **34**, 296.
[16] *Zeitsch. physiol. Chem.*, 1914, **93**, 316, 339.
[17] *Compt. rend., Carlsberg*, 1914, **11**, 45.
[18] *J. Inst. Brewing*, 1915, **21**, 344; *J.*, 1915, **34**, 628.

found to have very little proteolytic power, but pronounced peptolytic power.

T. Bokorny[19] shows that the action of yeast on animal and vegetable proteins for nine days gives rise to the formation of albumoses and peptones.

Carboxylase.—In 1914 C. Neuberg observed the presence of an enzyme in v. Lebedeff's yeast maceration juice[20] which had the power of fermenting pyruvic acid. In a paper[21] he finds that maceration juice can be prepared by drying yeast at 25° C., powdering and digesting it for two hours with water at 40° C.[22] He found that the juice from top fermentation yeasts contained carboxylase, but no zymase. Bottom fermentation yeasts yielded both enzymes. It was found also that in yeast maceration juice which had been dialyzed until it no longer fermented sugar, the carboxylase retained its full activity. The fermentation of pyruvic acid by maceration juice was found to proceed best in presence of amphoteric substances. In conjunction with E. Schwenk,[23] this author observed that the activity of maceration juice from which the co-enzyme had been removed might be restored by the addition of a mixture of the potassium and calcium salts of several (not one) α-ketonic acids and disodium phosphate. Neuberg and Ringer[24] show that yeast maceration juice converts α-ketoglutaric acid into succinic acid.

Zymase.—M. Oppenheimer[25] shows that yeast maceration juice contains small quantities of lactic acid, which increase when the juice is kept for several days under aseptic conditions. Addition of 1 gram of dextrose, dihydroxyacetone, or glyceraldehyde to 100 c.c. of the fresh juice increased the quantity of lactic acid formed by a maximum of

[19] *Allg. Brau. und Hopfenzeit.*, 1914; *J. Inst. Brewing*, 1914, **22**, 384.

[20] *See J.*, 1911, **30**, 147.

[21] *Biochem. Zeits.*, 1915, **71**, 1; *J.*, 1915, **34**, 1265.

[22] M. W. Beijerinck and J. J. Van Hest (*Folia Microbiologica*, *Holländische Beiträge zur ges. Microbiol.*, 1916, **4**, No. 2) state that in their experience the following method gave a maceration juice of highest fermenting power:—Beer yeast, without being pressed, is added to a 10 % solution of sucrose and left to ferment at ordinary temperatures. The yeast crop is pressed and then squeezed through a hair sieve, and, after being spread on filter paper in as finely granular form as possible, it is allowed to dry in a warm chamber. The dry mass is again sifted, and thus separated into floury and granular fractions. The flour contains a higher proportion of open cells than the granules, and yields a maceration juice of higher fermenting power. The large granules, in fact, give a juice which is quite inactive.

[23] *Biochem. Zeits.*, 1915, **71**, 135; *J.*, 1915, **34**, 1266.

[24] *Ibid.*, 1915, **71**, 225; *J.*, 1915, **34**, 1266.

[25] *Z. physiol. Chem.*, 1914, **89**, 45, 63; **93**, 233; *J.*, 1914, **33**, 156; 1915, **34**, 441.

0·23 gram. Sodium pyruvate, on the other hand, lessened the production of lactic acid. The author concludes that lactic acid is formed from sugar during fermentation by yeast juice, and that its immediate precursor is probably glyceraldehyde. Fresh yeast juice contained 0·17–0·25 % of glycerol. Addition of 1 % of dextrose, dihydroxyacetone, or glyceraldehyde increased the quantity of glycerol as follows: 3–12 % of the added dextrose, 9–15 % of added glyceraldehyde, and 11–19 % of added dihydroxyacetone. The addition of 0·1 % of sodium pyruvate to a 1 % solution of dextrose in yeast maceration juice increased the evolution of CO_2 sevenfold during the first hour, and raised the total volume of the CO_2 to the theoretical quantity in twenty-four hours (cp. Fernbach, p. 252).

Reductase.—It was observed by E. Buchner and his colleagues in 1903 that yeast possessed strong reducing properties, *e.g.*, towards methylene blue, and the same applies to zymin, the reducing power appearing to run parallel with the fermenting power. A. Harden and R. V. Norris,[26] continuing their work on the restoration of the reducing power of v. Lebedeff's washed dried yeast, found that a number of oxidizable substances may act as acceptors for the oxygen activated during the reduction process. On the other hand, many easily oxidizable substances—*e.g.* quinol—are without effect. The authors find that lactic acid restores the power of reduction, and is itself oxidized in the reaction, yielding acetaldehyde not in amount, however, equivalent to the lactic acid lost. It is suggested that the lactic acid is first converted into pyruvic acid, which is then transformed by the carboxylase of the yeast into acetaldehyde and carbon dioxide.

S. Lvoff[27] finds that the addition of phosphate increases the reducing power of yeast.

W. M. Bayliss[28] shows that urease, lipase, emulsin, lactase, papain, peroxidase, and catalase are active in media from which they may be removed by filtration through paper, the filtrates being inactive.

L. Adler[29] employed Sörensen's formaldehyde titration method for the estimation of amino-acid and polypeptide nitrogen in barley, malt, and beer. He states that the reaction with formaldehyde which is reversible becomes practically complete when a sufficient excess of formaldehyde is employed and the nitrogen compound is present in a solution N/10 strength with a concentration of hydrogen ions $P_H = 9$. Phenolphthalein was used as indicator. The method may be rendered

[26] *Biochem. J.*, 1915, **9**, 33; *J.*, 1915, **34**, 1107.
[27] *Biochem. Zeit.*, 1914, **66**, 440.
[28] *J. Physiol.*, 1915, **50**, 85.
[29] *Zeit. ges. Brau.*, 1914, **37**, 105, 117, 129; *J.*, 1914, **33**, 367.

more useful by carrying out the titration in stages, as suggested by Henriques and Gjalbaek.[30]

Biology and Physiology.

Barley.—H. C. A. Vine,[31] dealing with some characteristics of the endosperm of Chevallier and Goldthorpe barleys, points out that in sections of the former the cells adjacent to the aleurone layer are filled with starch granules of varying size, which merge gradually into the larger granules of the interior cells, whilst in Goldthorpe the tendency is for the cells near the aleurone layer to contain small and more uniform granules. The author cites numerous measurements of the diameter of granules in support of his argument. He also gives a great many well-executed drawings.

A. Mann and H. V. Harlan[32] have conducted a long series of useful experiments on the morphology of the barley grain with reference to enzyme-secreting areas. This work tends to clear up many conflicting statements in the literature, and it indicates the morphology of an ideal grain of barley for malting purposes to suit American requirements. Such work as this, guided by Mendel's law of inheritance, is most valuable in the production of varieties of barley best suited for the brewer's purpose. In this connection attention may be drawn to the proposed standards for barley grading in America.[33] It would serve no useful purpose to enter into a detailed account of the contents of this Bulletin. It should prove suggestive to our own Board of Agriculture in drawing up similar standards to suit our own conditions.

Hops.—Continuing his useful experiments on the characteristics of seeded and seedless hops, E. S. Salmon[34] finds that whilst the latter contain more resins, the former, on account of better growing out, produce more resins per acre. He states that the seeds do not impart an undesirable flavour to beer. The same author[35] describes a new variety of hops, the "Foundling." This hop has proved remarkably resistant to attacks of the disease known as "nettle-head," "skinkly," or in (Sussex) "silly hill," which has been attributed to the presence of the eelworm (*Heterodera schachtii*). It would also appear that the

[30] *Zeits. physiol. Chem.*, 1911, **75**, 363.
[31] *J. Inst. Brewing*, 1914, **20**, 23.
[32] Bull. No. 183, U.S. Dept. Agric.; *J.*, 1916, 375.
[33] Barley Bull. No. 2 of the Bureau of Barley and Hop Industry; *J. Inst. Brewing*, 1914, **20**, 722.
[34] *J. Board Agric.*, 1914, **20**, 953; **21**, 22, 123.
[35] *Ibid.*, 1915, **22**, 136.

"Foundling" is not liable to severe attacks of "blight" (*Aphis*). It is, however, about as susceptible to mould as most varieties of hops. The "Foundling" is a late hop with a green bine ripening about ten days later than the Canterbury white-bine. From the resin content, 10–12 %, it is judged that the "Foundling" hop is above the average in its preservative value.

J. Schmidt[36] has propagated in the garden of the Carlsberg Laboratory since 1911 clones, *i.e.*, groups of plants derived originally from one individual by cuttings, of Saaz, Bohemian, Oregon Clusters and New York Spaulding Clusters, the last two possessing a very pronounced aroma like that of turpentine. Clone plants have up to the present retained their properties, including aroma, unimpaired, so that the aroma of hops appears to be much less dependent on purely local conditions than has been generally supposed. Crossing experiments made with the two American plants and Danish males show that the characteristic aroma of the former was transmitted to between one-half and three-quarters of the offspring. This paper should be read in conjunction with Salmon's work, and more especially a recent paper by him,[37] which will be dealt with in a later report.

F. Rabak[38] has conducted a useful study on the volatile oil of hops in relation to the geographical source of the hops. His experiments confirm and extend those of A. C. Chapman.[39] The oil is found to consist of myrcene (30–50 %), humulene (15–25 %), and œnanthylic, caprylic and pelargonic esters of myrcenol (20–40 %). There were also found to be present traces of valeric, formic and heptoic acids besides formaldehyde, myrcenol, and sesquiterpene alcohols. In the ascending order of their ester content the hops investigated may be arranged thus, Bohemian, Californian, Washington, New York and Oregon. It may be recalled that A. J. Brown and his colleagues[40] found that Oregons were the highest as regards their preservative value.

A. C. Chapman[41] has investigated a number of samples of hops in order to ascertain the nature and quantity of their nitrogenous constituents. He finds that they contain 1·72–4 % of nitrogen, of which 0·44–0·9 % is in a form soluble in hot water. The average composition of the

[36] *Compt. rend. Carlsberg*, 1915, **11**, 149, 165, 184, 188; *J. Inst. Brewing*, 1915, **21**, 201, 452.

[37] *J. Inst. Brewing*, 1917, **23**, 60.

[38] Dept. of Agric., Washington, *J. Inst. Brewing*, 1915, **21**, 75.

[39] *J.*, 1893, **12**, 783; 1895, **14**, 63; 1898, **17**, 486; 1903, **22**, 509.

[40] *J.*, 1911, **30**, 102; 1913, **32**, 620.

[41] *Trans. Chem. Soc.*, 1914, **105**, 1895; *J.*, 1914, **33**, 879.

soluble portion on the dry hops was as follows :—Proteins and albumoses (0·046), ammonium salts and amides (0·1), amino-substances (0·095), bases and unclassified nitrogen precipitated by phosphotungstic acid (0·218), unclassified nitrogen not precipitated by phosphotungstic acid (0·037). Aspartic acid, potassium nitrate, and probably arginine are present. He states that cultivated hops contain at most only traces of morphine, which can have no physiological significance.

Yeasts.—Lichtenstein-Rosenblatt[42] shows that rabbits into which intravenous cultures of various yeasts have been injected yield blood sera which by means of the agglutination method serve to distinguish the various yeasts. It is possible in this way not only to discriminate between different saccharomycetes (top and bottom fermentation yeasts), but also to distinguish torulæ from yeasts.

Within recent years observations have been made tending to show that sugar may be assimilated by yeast which does not ferment it. Thus Lindner and others have shown that maltose is the most readily assimilated of all the sugars by yeast, even by those such as *S. exiguus* which do not contain maltase. These observations do not accord with the view that the assimilative and fermentative activities of organisms are due to the enzymes they elaborate, and A. J. Kluyver[43] has refuted them by showing that the maltose used contained nitrogenous matter, dextrin and dextrose. W. A. Davis[44] confirms Kluyver's results, and shows that Kahlbaum's preparation of maltose which was used by Lindner contained both dextrin and dextrose.

J. Crolbois and C. Ukmar[45] find that both yeast and bacteria are destroyed by ozone, the yeast being slightly more resistant than the bacteria. They conclude that yeast can be freed from a relatively small proportion of bacteria by ozonized air, but if strongly infected this treatment is ineffective.

An interesting observation has been made by R. de Fazi[46] that ultra-violet rays, which are well known to have a high bactericidal power, stimulate the activity of yeast as regards alcoholic fermentation by removing any bacteria present.

C. Neuberg and E. Schwenk[47] point out that if living yeast is kept in air-tight boxes at 5–10° C. it is found to contain both acetaldehyde and ethyl alcohol. By the autolysis of both fresh and dried yeast in

[42] *Woch. Brau.*, 1914, **31**, 293.
[43] *J.*, 1913, **32**, 803.
[44] *Chemical World*, 1914, **3**, 271 ; *J.*, 1914, **33**, 1068.
[45] *Ann. Brass. et Dist.*, 1914, **17**, 13.
[46] *Annali Chim. Appl.*, 1915, **4**, 301 ; *J.*, 1916, 191.
[47] *Biochem. Zeits.*, 1915, **71**, 126 ; *J.*, 1915, **34**, 1266.

water saturated with carbon dioxide an increase in the content of aldehyde and alcohol could be detected.

Fermentation.—In connection with alcoholic fermentation it will be remembered that Buchner and Meisenheimer expressed their adherence to v. Baeyer's hypothesis that lactic acid is probably an intermediate product in the fermentation of sugars. This hypothesis was subsequently refuted by Slator, who showed that lactic acid, even in concentrations insufficient to prevent the fermentation of glucose, is not fermented to any considerable extent by yeast. It was finally disproved by a very careful series of experiments by Buchner and Meisenheimer themselves. A. Fernbach has summarized his researches on this subject.[48] His experiments go to show that pyruvic acid may be regarded as an intermediate compound in alcoholic fermentation. It has been proved that pyruvic acid can be isolated from the products of the incomplete fermentation of sugars, and that it is easily convertible into alcohol by yeasts. It is suggested that the lactic acid found among these products may be formed by the reducing action of yeast on pyruvic acid.

In a paper on the Free and Combined Organic Acids in Wort and Beer, W. Windisch and K. Ten Doornkaat Koolman,[49] in comparing worts and beers, show that the effect of fermentation is to increase the acidity of the liquid to litmus and rosolic acid, and also to increase its alkalinity towards methyl orange. It is interesting to note in the authors' observations that a wort rich in basic substances owing to the use of a water of high carbonate content, stimulates the yeast to produce acids. In the titration of wort or beer with alkali in the presence of phenolphthalein or rosolic acid, the results are affected by the presence of phosphates, proteins or their hydrolytic products, which are of an amphoteric nature, as well as of certain salts of organic acids, which are neutral towards vegetable colouring matters like litmus, but are acid towards phenolphthalein and rosolic acid. Titration in presence of methyl orange indicates the quantity of bases combined with organic acids besides those present as phosphates of the types R_2HPO_4 and R_3PO_4.

Technology.

Malting.—In a paper by Schjerning[50] there are many points connected with the principles of the malting process which are deserving of attention. It must be remembered, however, that the experimental

[48] *J. Inst. Brewing*, 1916, **22**, 354; *J.*, 1916, **35**, 859.
[49] *Wochensch. Brau.*, 1914, **31**, 225, 235, 252, 275, 303, 311; *J.*, 1915, **34**, 441.
[50] *Loc. cit.*, p. 246.

data cited were obtained in the laboratory and not in the malting. The author deals chiefly with the conversion of the proteins of the grain and the development of the proteolytic enzymes. He states that over- or under-steeping weakens the proteolytic power, and leads to incomplete conversion of albumin 11 (edestin) into albumin 1, and of the latter into peptic products. Under-steeping fails to develop properly the latent powers of the barley for respiration and root growth, whilst over-steeping weakens these powers, and also those effecting saccharification, but it increases the production of acid and promotes rapid growth. The minimum steeping period, which enables the barley to take up sufficient moisture for normal germination, is 48 hours. A barley for which the normal steeping period is less than this is liable to undergo incomplete protein transformation. A barley which attains its maximum germinative energy after 24 hours' steeping is of doubtful value for brewing. The germination temperature most favourable to the proteolytic changes lies between 55° and 63° F. At higher temperatures they are retarded, and at 79° F. conversion of albumin 11 into albumin 1 and of the latter to peptic products is retarded more than conversion of insoluble protein into albumin 11, so that the last-mentioned substance tends to accumulate. Transformation of carbohydrates is most extensive at 68° F., respiration or physiological oxidation at 79° F., and root growth at about 68° F., though during the first four days it is most rapid at about 79° F. The greatest amount of carbohydrate and protein transformation usually occurs during the first four days, and the transformations may be considered as complete in ten days at 57–68° F. Decomposition of albumin 11 is not complete in ten days at 79° F. Excessive moisture during germination lessens transformation of carbohydrates and proteins, respiration, root growth and production of acid, and also lowers the yield of extract; most of these effects are also produced by insufficiency of moisture. Insufficient aeration affects the whole mechanism of germination and gives rise to a tendency for the accumulation of albumin 11. The influence of light is to accelerate the production of a state of over-germination. The proteolytic changes which take place on the kiln are very slight. Some coagulation of soluble albumins occurs above 194° F. The undesirable albumin 11, when present owing to abnormal germination, can be eliminated at temperatures above 149° F., the more quickly the drier the malt, the higher the temperature, and the greater the access of air to the malt. During storage the proteins of malt undergo little change; acidity and yield of extract increase slightly.

In connection with the production of colour and flavour of malt by

the kilning process, the writer, basing his views on the manufacture of caramel by the ammonia process, pointed out[51] that when green malt is held for several hours while still containing 10–15 % of moisture, the amino-compounds form combinations with the carbohydrates containing free carbonyl groups, and that when such compounds are heated to the final curing stage they are decomposed, giving rise to colour and flavouring matters. If the malt is not held at the critical temperatures in presence of sufficient moisture, the requisite colour and flavour are not produced. It was pointed out that the early stages of kilning malt, and not necessarily the final (curing) stage, determined the character of the malt, *i.e.*, whether it should be a pale or dark malt. These observations have been confirmed by Maillard,[52] who has denoted the compounds in question, "Melanoidenes," by C. J. Lintner,[53] by T. Langer,[54] and by W. Ruckdeschel.[55]

Brewing.—A new brewing process was patented by H. B. Wooldridge,[56] and its working on a practical scale is described by the writer and H. B. Wooldridge.[57] The brewing is conducted as usual until mash-tun taps are set. The wort is then run into a closed copper vessel and *boiled* under a pressure of 6 lb.[58] to the square inch for fifteen minutes with the desired quantity of sugar and hops. The pressure is gradually reduced to a quarter of a pound to the square inch, and the vessel is then connected with a vacuum pump, so that the wort is boiled, cooled and concentrated at a continually diminishing temperature. During this method of cooling the wort is in a continual state of violent ebullition, and the temperature may be maintained at any desired point for any length of time, by turning on the necessary amount of steam. The authors point out that the process affords the best possible means of agitating a wort between 120° and 80° F., which has been shown by H. T. Brown[59] to be necessary to ensure efficient "break" or "flocculation" of wort. The authors show that the process possesses economic advantages over the ordinary method of brewing, that it ensures freedom from contamination with air-borne germs at the most critical stage in the production of beer, whilst the hop extraction is quite

[51] *J. Inst. Brewing*, 1908, **14**, 514; *J.*, 1908, **27**, 1033.
[52] *Compt. rend.*, 1912, 154, 66; *J.*, 1912, **31**, 144.
[53] *Zeit. ges. brauw.*, 1912, **35**, 545, 553.
[54] *Alg. Zeits. Bierbrau. Malzfabr.*, 1914, **42**, 33.
[55] *Zeit. ges. brauw.*, 1914, **37**, 430, 437; *J.*, 1915, **34**, 192.
[56] Eng. Patent, 1910, 16744.
[57] *J. Inst. Brewing*, 1914, **20**, 81; *J.*, 1914, **33**, 329.
[58] Actual ebullition is essential, and this is effected by keeping up the steam pressure, and at the same time allowing some escape of steam.
[59] *J. Inst. Brewing*, 1913, **19**, 84; *J.*, 1913, **32**, 442.

normal, and the beers produced are superior in many respects to those brewed in the usual manner.

The employment of a converter and a filter press in place of an ordinary mash-tun with a false drainage bottom has been advocated for many years, and various forms of presses have been devised for the purpose. The disadvantage of this procedure has been a tendency for the mash to clog in the press, thereby causing much delay in working. Within recent years, however, special presses have been devised by which this difficulty is surmounted. Among these may be mentioned the German Weigel Press and the American S.B.B. Press. In the case of the former it has been asserted that after mashing is complete in the closed mashing vessel the whole of the first wort can be drawn off in twenty minutes, at the end of which time the press is filled with the goods, and washing out can be commenced. L. Briant, H. Harman, and C. Vaux[60] have given their experience with a mash filter of the Weigel type installed in this country. They confirm the Continental experience with the machine, namely that there is not only considerable saving of time in exhausting the goods, but that a more complete exhaustion is obtained. Thus, with a first wort of a specific gravity of 1089·4 the last runnings from the filter had a specific gravity of 1002·8 in one hour forty-five minutes, whilst those from the ordinary mash-tun and under similar conditions had a specific gravity of 1003·9 in three hours thirty minutes. So far as the writer is aware, no experiments with the S.B.B. filter are on record in this country.

A useful paper on Chilled Bottled Beers has been published by A. Hadley.[61] A rapid process is described whereby a beer is conditioned and dry hopped in a glass-lined or copper vessel. A quick-chiller of the counter-current type is placed between the conditioning and chilling vessels, whereby the beer can be cooled to 35° F. before entering the chilling and carbonating vessels in which its temperature is still further reduced, *e.g.*, to 28° F. It is pointed out that continuous carbonation is working satisfactorily in a number of breweries. The chilling is kept entirely separate from the carbonating, and the chilled beer is pumped through the carbonator, which is placed either between the chilling plant and the filter, or between the chiller and the filling machines. This arrangement is said to give more uniform results, whilst the beer is kept in a quieter condition for bottling.

J. L. Baker and H. F. E. Hulton[62] show that when sucrose and invert sugar solutions are added to beer as a priming, the rate of fermentation

[60] *J. Inst. Brewing*, 1914, **20**, 1; *J.*, 1914, **33**, 212.
[61] *Ibid.*, 1914, **20**, 504; *J.*, 1914, **33**, 1104.
[62] *Ibid.*, 1914, **20**, 242; *J.*, 1914, **33**, 562.

is practically identical in both cases, although it is well known that sucrose is not directly fermentable. It is pointed out in explanation of this that beer at racking contains more or less yeast which will convert sucrose into invert sugar. In further explanation of this phenomenon, the writer would point out that A. Bau showed some years ago that beer invariably contains invertase unless it has been pasteurized. The same author has shown more recently[63] that beer contains not only invertase but also melibiase and amygdalase.

Wine.—Only one paper on this subject calls for special mention, namely that by H. T. Brown, who for several years has owned a vineyard in South Africa. He gave an account[64] of his studies on the white wines of South Africa during a visit. He refers specially to the liability of these wines to *casse* or turbidity, accompanied or preceded by an increase in colour, and a more or less bitter flavour, and a characteristic earthy odour or *terroir*. The essential conditions for the appearance of this disease were found to be access of oxygen, the presence in the wine of traces of iron salts which act as carriers of oxygen, and of certain oxidizable substances, notably tannic acid. No connection was noted between this *casse ferrique* and the presence of oxidases in wine, but it is pointed out that the higher alcoholic strength of South African wines as compared with European, favours the disease, and Brown is of opinion that a reduction of the gravity of the must to about that of European wines would tend to improve the character of these wines, and he urges the repealing of the South African law which prohibits the suggested dilution of the wines and the addition of citric acid, which latter is shown to act as a preventive of *casse ferrique*.

Distilling.—It will be remembered that about the year 1892, Calmette isolated a mucor to which he gave the name *Amylomyces Rouxii*, which had been used for many centuries in China for the production of alcohol from rice. By means of this organism starch may be saccharified and fermented in one and the same vessel, and the process, known as the Amylo Process, had been at work up to the period of the War at Seclin. An interesting account of this process is given by O. Grove.[65] One of the difficulties encountered has been the invasion of the vats by other organisms, and this in spite of the fact that they are covered in. However, H. Boulard[66] has isolated a mould which he designates "Mucor Boulard No. 5," which can be used in the Amylo Process, and

[63] *Woch. Brau.*, 1915, **32**, 189; *J.*, 1915, **34**, 1025.
[64] *J. Inst. Brewing*, 1914, **20**, 345; *J.*, 1914, **33**, 762.
[65] *Ibid.*, 1914, **20**, 248; *J.*, 1914, **33**, 562.
[66] Fr. Patent, 1913, 464601; *J.*, 1914, **33**, 497.

is so robust that bacterial infection is not to be feared, and saccharification can be carried out in open vats at temperatures as high as 114° F., or as low as 68° F.

Baker's Yeast.—At the present time the manufacture of an increased quantity of yeast for bread making is a problem of increasing urgency, and on this subject a paper has been published by A. C. Reavenall.[67]

Analysis.—Unquestionably the most important work under this section of the subject is the publication of a series of five reports by Sir Edward Thorpe and Dr. H. T. Brown,[68] giving the results of their investigations in drawing up tables for the determination of the original gravity of beers by the distillation process. The products of numerous breweries throughout different parts of the country, produced under different conditions and from different materials, were most thoroughly investigated, and as a result of this, what is denoted in the Reports as the Mean Brewery Table has been made official by Act of Parliament, under Section 7 of the Finance Act of 1914, in replacement of the older, less accurate table.

T. H. Pope[69] recommends the use of Mailligand's ebullioscope for the more rapid estimation of the original gravity of beer. This instrument had been previously recommended by J. C. Cain[70] for the estimation of alcohol.

Water.—Some useful suggestions have been made as regards the estimation of salts in brewing waters by W. Windisch, C. Ten Doornkaat Koolman, and H. Krumhaar,[71] especially as regards the combination of the positive and negative ions. The suggestions are based on a study of the change in composition of a water after softening with lime. The authors cite a water showing the following oxides and acid anhydrides in parts per 100,000 :—CaO 17·4 ; MgO 9·8 ; CO_2 16·3 ; SO_3 15·2. These would be combined according to the usual method and the suggested method as follows :—

	$CaCO_3$.	$MgCO_3$.	$CaSO_4$.	$MgSO_4$.	NaCl.
Old method	12·5	20·6	25·6	0·0	2·6
New method ...	26·4	5·9	0·9	21·0	2·6

[67] *J. Inst. Brewing*, 1915, **21**, 97.
[68] *Ibid.*, 1914, **20**, 569.
[69] *Brewers' Journal*, 1914, **50**, 239 ; *J.*, 1914, **33**, 496.
[70] *Chem. News*, 1914, **109**, 37.
[71] *Woch. für Brau.*, 1914, **31**, 65, 73, 85, 93 ; *J.*, 1914, **33**, 369.

They claim that the new method shows much better than the old how the water will behave on softening.

In a subsequent paper W. Windisch and C. Ten Doornkaat Koolman[72] describe simple methods for the rapid volumetric estimation of salts in brewing waters.

Carbohydrates.—The writer has found that Ewers' acid hydrolysis method of estimating starch[73] gives very fair results in substances which contain no other compounds changing their optical rotation on treatment with acids under Ewers' conditions. In the case of cereals and other materials containing pentosans, for the effect of which it is impossible to correct, the taka-diastase method of Davis and Daish[74] is the most accurate yet devised. Davis has published a summary of the work carried out by himself and his colleagues on the use of enzymes and special yeasts in the analysis of carbohydrates.[75]

The writer[76] has shown that raw beet products contain a much larger percentage of nitrogenous substances than do raw cane products of the same sugar content. He points out that betaine and other trimethylamine derivatives, as well as citrazinic acid, are present in raw beet products and that the presence of these substances may account for the unsuitability of raw beet products as brewing sugars.

Hops.—O. Neumann[77] shows that when hops are boiled with light petroleum the bitter substances are extracted to the same extent as by boiling wort. He defends the method of estimating the bitter substances by titration of the petroleum extract with alkali. R. Seibriger[78] urges the advantage of the use of cold carbon tetrachloride in extracting hops, since it dissolves the so-called γ-resin, which is insoluble in petroleum. He recommends this method of extraction for the estimation of the bitter principles of hops.

J. Schmidt, Ö. Winge and J. P. H. Jensen[79] state in a very long and comprehensive paper that the so-called γ-resin should not be ignored, as it confers a certain bitter flavour to wort and promotes coagulation of the proteins. The bitterness values of the α-, β-, and γ-resins are said to stand approximately in the proportion 10 : 7 : 4. The method of analysis they suggest is as follows:—The hops (15 grams) are disintegrated in a mincing machine, dried *in vacuo* over sulphuric acid

[72] *Woch. für Brau.*, 1914, **31**, 131.
[73] *Zeit. öffentl. Chem.*, 1908, **14**, 150; *J.*, 1908, **27**, 238.
[74] *J. Agric. Science*, 1914, **6**, 152; *J.*, 1914, **33**, 657.
[75] *J.*, 1916, **35**, 201.
[76] *J. Inst. Brewing*, 1914, **20**, 185; *J.*, 1914, **33**, 433.
[77] *Woch. für Brau.*, 1913, **30**, 516.
[78] *Ibid.*, 530, 610.
[79] *Compt. rend. Carlsberg*, 1914, **11**, 116.

at 35° C., and extracted by remaining in contact for an hour with dry ether free from alcohol (500 c.c.), the residue being washed with a further 100 c.c. of ether. The ether extract is titrated with N/20 potassium hydroxide and phenolphthalein: 1 c.c. = 0·4 gram of resin.

W. Wölmer[80] finds that α-bitter acid (humulone) has the composition represented by the formula $C_{15}H_{22}O_4$. By the action of sodium hydroxide on this acid there are formed acetic and humulinic acids, a saturated acid $C_6H_{10}O_2$, and isobutyraldehyde. It is considered probable that this aldehyde is formed when wort is boiled with hops.

[80] *Zeit. ges. Brauw.*, 1915, **38**, 394.

WATER PURIFICATION AND SANITATION.

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The questions of the supply of wholesome water in sufficient quantity for the maintenance of a high standard of health and cleanliness in domestic and urban life and the purification of that water after use—viz., sewage disposal—are complementary problems. The evidence in favour of the advantages of the water carriage system for ridding human resorts of undesirable waste matters is now overwhelming. It is notorious that as the quality of water supplied improves the quantity consumed per head of population tends to rise. Thirty years ago the amount per head was but a few gallons, whereas to-day many large towns supply 20–30 gallons per head, and the Metropolitan Water Board supplies about 36 gallons per head, whilst in many American cities the extravagant amount of 200 or more gallons is a common figure.

The Blue Book, "Water Undertakings in England and Wales," issued in 1915, shows the general state of affairs in this country as regards water supply and shows that polluted and uncontrolled supplies are still much used. The pressing need for controlling consumption of water is illustrated in a paper by Messrs. A. B. E. Blackburn and Percy Griffiths, read before the Institution of Water Engineers, December, 1915.[1]

The treatment of water by slow sand filtration has been in vogue for nearly 100 years, and the efficiency of such filters in reducing the organisms of a dangerous character has been increasingly demonstrated in recent years. Financial and other practical considerations have favoured the increasing use during the past ten years or more of mechanical filters combined with preliminary treatment of the water by means of precipitants, and they are now widely used in America, and even in this country. At St. Louis a plant for treating 160,000,000 galls. per day and at Baltimore for treating 128,000,000 galls. per day have been installed, whilst at Sheffield, Huddersfield,

[1] See *Surveyor*, Dec. 17th and 31st, 1915.

Shrewsbury, York, and other places substantial installations are at work.

The Puech-Chabal system, originating at Paris for treating the water of the Seine, appears to have considerable advantages where turbid waters are to be treated, and this system consists in the use of multiple filters, the primary or roughing filters consisting of coarser sand or gravel followed by fine sand filters. In this system it is claimed that the final filters may be run for many months without cleansing. The modern tendency is towards a persistent use of germicidal agents—*e.g.*, hypochlorites (chiefly calcium hypochlorite), chlorine, lime, or ultra-violet rays—and it would seem that the use of such antiseptics coupled with rapid filtration is likely to become a settled practice.

For a detailed discussion of the respective merits of these modern systems the following papers may be consulted: "Theory and Practice in the Filtration of Water," by Walter Clemence[2]; "Value of Mechanical Filters in the Purification of Water," by Thos. Vee[3]; "Treatment of Water with Hypochlorite," by Joseph Race.[4] Dr. Houston advocates lime treatment to save storage and expedite filtration.[5]

Treatment by ultra-violet rays appears to be very effective, even for turbid waters, and does not present the difficulties arising from overdosing with lime, chlorine, etc.[6] The cost of treatment appears to be high, but little definite information thereon is at present forthcoming, although its use finds some favour amongst French engineers.

Amongst all the belligerent armies the treatment of water for drinking purposes by means of calcium hypochlorite in the field seems to find general favour because of the ready way in which it can be applied to both large and small quantities of water. See paper on "Purification of Drinking Water by Means of Calcium Hypochlorite," by H. Vincent and Guillard.[7] Compressed tablets, each containing 0·015 grm. of hypochlorite (3·5 mgrms. available chlorine) and 0·08 grm. of sodium chloride are prepared, and one tablet is used for each litre of water; the water is fit to drink in 20 minutes time. *B. coli* are killed by this treatment in 10–12 minutes, even when much organic matter is present.[8]

[2] *Surveyor*, April 21st, 1916, 418; *J.*, 1916, 650.

[3] *J. Roy. San. Inst.*, June, 1915.

[4] *J.*, Sept. 30, 1915, 931; see also *J.*, 1912, 611, and *Surveyor*, 1915, 577.

[5] See *Met. Water Board Reports*, also *Report on Aberdeen Water Supply*.

[6] See *Report of Board of Health of Ontario*, March, 1916.

[7] *Comptes rend.*, 1915, **160**, 483–486; *J.*, 1915, 569.

[8] See also Guillaumin and Vienne, *J. Pharm. Chim.*, 1915, **12**, 377–387; *J.*, 1916, 66.

Sewage Disposal.

During the last twenty years or so the art of purifying sewage has undergone considerable development, so that now a much larger choice of methods is available to those charged with the duty of disposing of town's sewage. This applies chiefly to the question of treating the liquid portions of the sewage, but the more difficult problem of dealing with sewage sludge is still in a much less satisfactory position.

Precipitation of the solids, with land treatment for the clarified liquor, was the standard method for very many years, and where plenty of good land is available, and rural surroundings obviate any serious nuisance, no more satisfactory mode of purifying the effluent and disposing of the solids is likely to be forthcoming.

The growth of population and of industry, the scarcity of good land in suitable and convenient sites, coupled with the inevitable and increasing dangers from more and more heavily polluted streams, made the question a very urgent one. Other means for dealing with the problem were sought, and during the last decade of the nineteenth century and the opening years of the twentieth century experimental investigation became the order of the day. The rival merits of the older precipitation and the newer septic tank process with the choice of "contact" beds or percolation beds for the sewage liquor, were put forward by enthusiastic supporters. As plants were laid down involving the outlay of much public money it became incumbent on each partisan to justify his choice, and the real issues were thus further confounded by interested and political considerations.

The matter was one of public urgency, and under these circumstances the Royal Commission on Sewage Disposal was appointed in 1898 to investigate and report upon the whole question in an impartial manner.

In July, 1901, the Commission[9] reported that it was possible to obtain sufficient purification of the liquid portions of the sewage by other means than land treatment, and the Local Government Board modified its regulations accordingly. Very wisely the Commissioners treated the question of methods with extreme caution, preserving always the correct scientific attitude of the open mind with regard to possible developments, and refusing to accede to the foolish clamour from some quarters for an authoritative statement as to the "best method" of sewage treatment; and whilst insisting on the fact that it was possible to purify sewage to any desired reasonable extent in various well-established ways, the choice of means was left to the local authorities under the supervision of the Local Government Board.

[9] *First (Interim) Report.*

The more recent developments in sewage disposal methods, which bid fair to entirely revolutionize sewage works practice, completely justify the attitude of the Commissioners throughout.

The combined result of the efforts of many workers in this country, on the Continent of Europe, and in America has tended by the inexorable logic of things to a sound and perfectly stable issue. The elements of the problem may be simply stated—viz., to purify foul and noxious liquids and to dispose of offensive solid matters without public nuisance and at reasonable cost. In general, the objective is to restore all rivers and streams to the "clean" condition, so that they shall absorb no more than 0·2 part per 100,000 of dissolved oxygen in 5 days at 65° F.[10]

The question of proper sanitation is paramount, and the recovery of materials from the waste products in sewage is simply accessory to this main issue; and exaggeration of the importance of recovering constituents of value, which is after all a secondary question, to the detriment of this main issue, by those who profess to speak with authority on this public question, is to be deprecated.

Owing to the great diversity of the waste matters to be dealt with in different places and the varying conditions obtaining in different localities, all responsible authorities recognize that each case must be considered on its merits. To translate this general principle into working practice the Commission from the very first recommended that the only feasible way of doing this was to set up Rivers Boards in various districts (similar to the West Riding of Yorkshire Rivers Board) with a central authority (a new department of the Local Government Board) whose decision should be final in cases of dispute; and the general consensus of opinion is in entire agreement with this recommendation.

The Commission published nine Reports with a final Report summarizing their recommendations and their work in the nine Reports. The ninth Report, dealing with "The Disposal of Liquid Wastes from Manufacturing Processes," is dated February 11th, 1915, as is also the final Report.

The nine Reports represent the work done by the Commission during 16 years. The first, second, fifth, and eighth Reports deal with the purification of domestic sewage discharging into streams, the fourth and seventh Reports with the discharge of sewage to tidal waters, and the third, sixth, and ninth Reports deal with manufacturing effluents.

Almost every aspect of the sewage problem has been dealt with in these

[10] *Eighth Report, Roy. Comm.*

Reports, and a most excellent summary is given by the Commissioners of their work in the final Report. A much needed guide[11] for those wishing to refer to items in the immense mass of detail in the Reports, by one of the members of the staff of the Commissioners, was published in 1915, and it strikes one that a guide so necessary might very well have been produced officially. In the space at our disposal only the briefest reference to some of the more salient questions dealt with by the Commissioners is possible.

Standards.—For effluents from manufacturing processes the Commissioners recommend not standards in the same sense as those suggested for sewage effluents, but rather, as they put it, "limits of impurity." It is stated clearly that this portion of the problem has of necessity been dealt with only partially and in an imperfect manner, and that the work is the proper province of their proposed central authority and River Boards, who will have the time and the means to investigate the multifarious details. With this proviso in mind much of the hostile criticism aroused by these Reports is discounted, not excepting a valuable and important criticism of this portion of the Commissioners work (ninth Report) made jointly by H. MacClean Wilson and H. T. Calvert.[12]

Inevitably on a question so controversial as that of standards the recommendations of the Commissioners have come in for much discussion. The question is a practical one, and as such calls for compromise so that a quite definite and workable line shall be drawn. Much of the criticism brought against the Commissioners is so unfair as to be either ill-considered or biassed by local and special considerations or to be due to merely interested motives. The standard of sewage effluents is 3·0 parts per 100,000 of suspended matter and 2·0 parts per 100,000 of dissolved oxygen absorbed in 5 days at 65° F. The reasons for adopting this particular standard are simply and clearly stated as the result of practical experience. The figure for suspended matter can be maintained without undue difficulty, and it was found that a river of "average purity" takes up 0·2 part per 100,000 of dissolved oxygen in 5 days at 65° F., and that so long as the figure 0·4 part of dissolved oxygen absorbed was not exceeded, no nuisance would result.

Experience further showed that in the great majority of cases the river volume was eight times or more than the volume of the effluent, so that by a simple calculation eight volumes of a 0·2 river mixed with 1 volume of effluent with 2 parts of dissolved oxygen absorbed per

[11] *Guide to the Reports, Evidence and Appendices of the Royal Commission on Sewage Disposal*, by G. B. Kershaw, P. S. King and Son, Ltd., Westminster, 1915.

[12] *Surveyor*, Aug. 27th, 1915, 228.

100,000 gave a resulting liquid absorbing not more than 0·4 part per 100,000—*i.e.*, the safe limit.

However, they insist that the governing factor must be the volume of river as compared with effluent and only so much purification insisted on as is essential in each case for safety.

Sludge Disposal.—Valuable as the work of the Commissioners has been in other respects, they practically leave the most troublesome portion of the sewage problem—viz., sludge disposal, where they found it. They describe in their customary cautious manner in their fifth Report, without bias, the existing processes for sludge disposal and with comparative costs, etc. In Appendix IV to the fifth Report they give some results of quantitative experiments upon sludge digestion in septic tanks, whilst in Appendix VIII to that Report and a Memorandum at the end of Volume II of the ninth Report they give the results of valuable experiments on the manurial value of sewage sludge.

It is hardly an exaggeration to say that the sludge problem is the sewage problem, for the bulk of the liquid portion of sewage is but a vehicle for transporting noxious solids away from human resorts. The problem is so difficult only because the sewage solids are offensive. The much used method of sludge pressing is very expensive, is offensive, and does not render the solids inoffensive, and merely reduces the volume of the sludge. Sludge trenching is very offensive, is not cheap, and often seriously impairs the land whilst furnishing an indifferent fertilizer.

The negative point brought out by the Commissioners as to the very low fertilizing value of sewage sludge is very useful in view of the attempts made to produce a marketable fertilizer from the sludge. The Commissioners found the dry sludge to be worth less than 10*s.* per ton in the field, and no process of preparation yet brought forward can suitably prepare the sludge for the land at anything approaching that low figure. In their ninth Report they state that de-greased sludge was even of less value than the natural dry sludge. Of the more recent work on separate digestion of the sludge as in the Imhoff tank, or in separate tanks, as at Birmingham[13] and elsewhere, they say nothing.

The Activated Sludge Process.—This process, introduced two and a half years ago by Messrs. Ardern and Lockett of Manchester,[14] is still in the experimental stage. It has aroused more attention than any other process for many years, as it proposes to bring about drastic and much

[13] *J.*, 1914, **33**, 3-9. [14] *J.*, 1914, **33**, 523.

desired changes in the methods of purifying sewage. Essentially the principle of the process is that of bringing the liquid to be purified into intimate contact with the proper kind of organisms in the presence of excess of air, exactly the same as that obtaining in any other efficient aeration process. But the method of doing this represents a profound modification of former practice. By blowing air in a suitable manner for a prolonged period through sewage sludge, the sludge alters its characteristics and becomes charged with "active" organisms capable of purifying sewage under aerobic conditions. This sludge so prepared is said to be "activated," and by introducing 25 %–30 % by volume of this sludge into a tank containing sewage and bubbling air freely through the mixture, the liquor is converted after a few hours into an innocuous liquid comparable in all respects to any good sewage effluent. So wide is the interest aroused that already the process has a voluminous literature of its own dealing with the work done in this country, Canada, and America.[15] Prof. Fowler states that the process is, in his opinion, to be entirely referred to bacterial activity. Others—viz., Dr. Bartow and Mr. W. D. Hatfield of Illinois University—found considerable quantities of the worm *Aeolosoma Hemprichi* and other organisms, and at one time attributed much of the purification to these organisms. It appears that the bulk of sludge actually increases as the operation proceeds, and the very high nitrogen content of the resulting sludge was attributed to the presence of enormous numbers of the bodies of these larger organisms. The process is said to include three principal operations—viz., a clotting or clarifying action, a rapid carbon oxidation, and, finally, nitrification. It is obvious the action may be stopped at any stage, but the latest observations indicate that the sludge deteriorates in activity unless the action is carried through to the nitrification stage.

The activated sludge installation at Worcester is the largest at present in this country, treating nearly 1,000,000 gallons per day.

By means of a pulsating device invented by Mr. J. A. Coombes, of Messrs. Jones and Attwood, Stourbridge, Mr. Ardern informs me that the air supply may be reduced to 7·5 cubic feet of free air per square foot of tank per hour, as against his original estimate of 15 cubic feet, and he expects to be able to reduce it still further. Moreover, his aeration period is now reduced to 3 hours.

A plant is to be constructed at Withington Works (Manchester) to

[15] See "The Activated Sludge Process of Sewage Purification," by G. J. Fowler, *J. Inst. San. Eng.*, March and April, 1916; also *J. Ind. and Eng. Chem.*, 1916, **8**, [7].

deal with 400,000 galls. per day. At Salford 150,000 galls. per day is treated both by "fill and draw" and continuous methods, and at Stamford, Lincoln, a plant is in operation treating 100,000 galls. per day of strong sewage, and good results are apparently being obtained at these places. The largest plant at work is at the City of Milwaukee, U.S.A., constructed by Mr. T. Chalkley Hatton to treat 2,000,000 galls. per day.[16] At Salford, Worcester, and Stamford the activated sludge plant has been adapted from previously existing works.

The claims recently put forward by W. Howarth, of Sheffield, to introduce aeration and agitation by mechanical means are not admitted by Messrs. Ardern and Lockett.

The mechanism used in the process varies somewhat, but the following will give some idea of that chiefly favoured at present.

The method of applying air, etc., is described in patents by Messrs. W. Jones and Jones and Attwood, Ltd.,[17] as follows:—

A series of diffusers spaced apart and each formed of a porous earthenware plate, on the underside of which compressed air is admitted, is arranged transversely across the bottom of each section of the tank holding the sewage to be aerated. The sewage is transferred from one section of the tank to the next by a circulator consisting of an uptake pipe, at the bottom of which compressed air is admitted; the mixture of air and sewage rises and is delivered into the covered top of a downtake pipe, into which air is also admitted below the water level. The lower end of the downtake pipe is enlarged to form a foot chamber, the excess of air escapes and is passed on to supply the diffusers, while the sewage passes into the bottom of the next section of the tank.

The following patents by G. W. and J. F. Naylor, Denby Dale, may also be referred to:—Eng. Pats. 20259, 20579, 23146, and 24386/1914; 9870 and 9989/1915.[18]

Other Methods of Sewage Disposal.

In a paper on "Sewage Disposal by Dilution," by Dr. Adeney, read before the Institute of Sanitary Engineers on Dec. 1st, 1915,[19] many points of interest and importance are brought forward, one practical

[16] *Engineering News*, July 15th, 1915; also *Engineering Record*, Oct. 16th, 1916.

[17] Eng. Pats. 22952/1913 and 729/1914, *J.*, 1915, 197, 244. Other English Patents by the same patentees are Nos. 19916, 22736, 22737, and 24630/1914, and 1141/1915, *J.*, 1915, 632; 1916, 195, 326.

[18] *J.*, 1915, 195, 314, 978, 1269; 1916, 615, 434.

[19] *J. Inst. San. Eng.*, Dec., 1915; *Surveyor*, 1915, **49**, 600.

point of the utmost importance being the greater power of rapid deoxidation of the river water possessed by putrid sludge as against fresh sludge. Obviously the method of dilution with proper safeguards is embodied in the recommendations of the Royal Commission on Sewage Disposal.

Since the publication of the ninth Report, B. Kershaw has published a series of papers in *The Surveyor*, dealing with various important trade wastes.

Claims have been put forward[20] as to the rapid purification of sewage by passing through a three-inch annular layer of sand, on to which the sewage is thrown with great force from a rapidly revolving disc on a central vertical axis. The arrangements are extremely ingenious, but the present writer found on testing this device on solutions of urine and fæcal matter that his results utterly failed to agree with the claims put forward by the inventor, and apparently his experience is the same as that of other disinterested investigators.

The Dickson sludge process for the preparation of a fertilizer from sewage sludge by fermenting the sludge with yeast at 90° F., thereby enriching the sludge with nitrogenous matter, and facilitating the removal of much of the water in the sludge, with subsequent drying in a dryer, is also very ingenious. The cost of this process is from 25*s.* to 30*s.* per ton of fertilizer, but, as both Dr. Rideal and the present writer pointed out in the discussion on the paper, the value of the dried sludge is unaltered and still remains at the figure given by Voelcker,[21] viz., 10*s.* per ton. This cardinal fact is not affected by the admixture of phosphates and potash as in their reinforced fertilizer "Manurito," and all these operations leave the question of the economic utilization of sewage sludge exactly where it was before.

At the International Engineering Congress held in San Francisco in the Autumn of 1915, Rudolph Hering read a paper entitled "The Disposal of Suspended Matter in Sewage."[22] The paper may be described as a review of the devices and methods adopted in both hemispheres during recent years to eliminate or avoid nuisance in the collection, conveyance, and disposal of offensive solids. The author is guilty of some important omissions and inaccuracies, as, for instance, those pointed out by Dr. Fowler in the *Canadian Engineer*.[23] Hering concludes that nuisance is entirely avoidable, and for sludge treatment places the issue between the activated sludge process (aerobic), which is still in the experimental stage, or inoffensive anaerobic treatment (Imhoff

[20] See E. H. Tripp, *J.*, 1915, **34**, 517.
[21] *Roy. Comm., Fifth Report.*
[22] *Surveyor*, 1915, **48**, 672.
[23] *Ibid.*, 1916, **49**, 405.

method) or separate digestion of sludge as at Baltimore and other places.

The broad point emphasized in Hering's paper is the now imperative demand, in the problem of sludge treatment, for an inoffensive means of producing an inoffensive end product at reasonable cost. The Imhoff method leaves the storm sludge (25 % or so of the whole) to be treated by some other means, and the only process in actual operation on a large scale which completely satisfies this requirement is the method of separate digestion of the sludge at Birmingham (England), where something like 8000 cubic yards of sludge per week are successfully and unostentatiously treated in this way. The fate of the sludge under the activated sludge process is not yet thoroughly determined. Its value as a fertilizer seems to be established, but the realization of this value is an economic question not yet solved, and those most interested in the process have high hopes of success.

Prof. Fowler has expressed the opinion that the solution of the sewage problem is to be found only along the lines which he and his colleagues, Messrs. Ardern and Lockett, have so ably exploited. The present writer would respectfully suggest that in a question of such importance and such wide public interest such generalizations are uncalled for and are but expressions of pious opinion biassed in favour of the plans with which Prof. Fowler is most intimately associated. From the point of view of the public, the sewage problem is simply a sanitary and economic problem, and that method of dealing with the sewage of a particular locality in an inoffensive fashion, with the least expense, is *the solution* of the problem from that community's point of view. For instance, in a town situated by a sufficient mass of water as the sea, a great river, or a great lake, the best solution will probably resolve itself into a question of engineering pure and simple, and the line of thought actuating the Royal Commission on Sewage Disposal is the only sound line, because it is the highest and broadest line treating the problem without any narrow prejudice.

For other minor developments, such as the S.O.S. method of recovery of products from sludge, various methods of converting sludge, garbage, etc., into fertilizers, methods of sterilizing sewage by electrolysis, etc., as in Elmhurst, America, the literature must be consulted. The patents taken out in England, France, Switzerland, Russia, Germany, and America are very numerous.

In the various military camps, expensive emergency devices have been used to treat or destroy sewage matters, and these have chiefly served to emphasize the overwhelming advantages of a water carriage system with proper means of treating the resulting liquids and solids.

Antiseptics.—Various investigations on water, sewage, and surgical treatment have served to indicate the germicidal value of substances of the chloroamine group (containing the $=NCl$ group), being more efficacious even than sodium hypochlorite.[24] The value of chlorine treatment is often due to the secondary action of chloroamines produced *in situ* as in wounds, etc.

[24] H. D. Dakin, *Proc. Roy. Soc.*, 1916, B. **89**, 232–251 ; *Comptes rend.*, 1915, **161**, 150–153 ; *J.*, 1915, 919, 977, and 1916, 651.

FINE CHEMICALS, MEDICINAL SUBSTANCES, AND ESSENTIAL OILS.

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This review deals with the subjects classified under the above heading in the order given. The recent synthetic applications of acetylene are first described. Then follows an account of the progress made with medicinal substances, synthetic and natural. Finally, the subject of essential oils is reviewed.

Preparation of Acetaldehyde, Acetic Acid, and its Derivatives from Acetylene.

A number of interesting reactions are described in recent patent literature by which acetylene can be converted into acetaldehyde, acetic acid, ethyl acetate, or acetic anhydride. They may be classified as follows:—

1. Acetylene→Acetaldehyde $CH{:}CH + H_2O \rightarrow CH_3{\cdot}CHO$
2. Acetaldehyde→Acetic acid $CH_3{\cdot}CHO + O \rightarrow CH_3{\cdot}CO_2H$
3. Acetaldehyde→Ethyl acetate $2CH_3{\cdot}CHO \rightarrow CH_3{\cdot}CO_2C_2H_5$
4. Acetylene→Acetic acid $CH{:}CH + H_2O + O \rightarrow CH_3{\cdot}CO_2H$
5. Acetylene + Acetic acid → Ethylidene diacetate → Acetic anhydride + Acetaldehyde

$$CH{:}CH + 2CH_3{\cdot}CO_2H \rightarrow (CH_3{\cdot}CO_2)_2CH{\cdot}CH_3 \rightarrow (CH_3{\cdot}CO)_2O + CH_3{\cdot}CHO$$

1. The hydration of acetylene to acetaldehyde is carried out in general by passing a stream of the gas into an aqueous solution of an acid in the presence of a mercury salt, and removing the aldehyde formed. The patents covering this reaction differ in their claims respecting the nature and concentration of the acid employed, the temperature at which the reaction is carried out, and the mode of removing the aldehyde.

A current of acetylene is passed into a solution of a mercuric salt in at least 45 per cent. sulphuric acid, or at least 25 per cent. phosphoric acid, at temperatures below 70°, preferably at ordinary temperatures,

when acetaldehyde and its condensation products and polymerides are obtained. The formation of further condensation products, such as crotonic aldehyde, is greater the higher the concentration of acid used. The process can be stopped at intervals in order to separate the products by distillation, or precipitation by a neutral salt, such as sodium sulphate.[1]

The subject matter of another patent[2] is similar, except that here a liquid which readily dissolves acetaldehyde, but which is insoluble in the mercury salt solution, may be added.

Further patents[3] claim the use of a mercury salt in a highly concentrated organic or mineral acid other than sulphuric or hydrochloric acid below 50°. The aldehyde may be extracted from the reacting solution by means of naphtha, etc., or the reaction may be carried out in the presence of an immiscible solvent.

Another means of collecting the aldehyde is to introduce the acetylene into a hot solution of a mercury salt, so that the aldehyde distils off as soon as it is formed.[4] Or, again, the reaction may be carried out at a temperature below the boiling point of acetaldehyde, but high enough for the aldehyde to be continuously carried over by the excess of acetylene. The aldehyde is washed out of the latter by water, and the acetylene passed into a second vessel.[5]

The most favourable condition for the formation of acetaldehyde from acetylene, mercuric oxide and sulphuric acid is found to be attained if the sulphuric acid is employed in the dilute state and not concentrated as previously supposed. The liquid should contain not more than 60 grams of sulphuric acid per litre, and the temperature should be kept well above the boiling point of the aldehyde—at 70°–80°. The yield is stated to be almost quantitative.[6]

A later patent, however, indicates that moderately concentrated acids should be used, the use of concentrated acids diminishing the rate of the reduction of the mercury salts to metallic mercury.[5] This reducing effect appears to be the cause of some trouble, and a method has been protected for impeding the separation of mercury by the

[1] Chem. Fabr. Griesheim-Elektron, Fr. Pat. 425057 (1911), *J.*, 1911, 923; also Eng. Pat. 29073 (1910), *J.*, 1911, 1088.

[2] N. Grünstein, Ger. Pat. 250356 (1910), *J.*, 1912, 1053.

[3] N. Grünstein, Ger. Pats. 253707 (1910) and 253708 (1911), addition to 250356, *J.*, 1913, 109.

[4] Consortium f. Elektrochemische Industrie, Fr. Pat. 460553 (1913), *J.*, 1914, 42.

[5] Chem. Fabr. Griesheim-Elektron, Fr. Pat. 474246 (1914), *J.*, 1915, 735.

[6] Consort. f. Elektrochem. Industrie G. m. b. H., Fr. Pat. 455370 (1913), *J.*, 1913, 959.

addition of a ferric salt, *e.g.*, the sulphate, or a compound of hexavalent chromium, *e.g.*, chromic acid, to the solution.[7]

Methods for the recovery of mercury from the deposited mercury sludge have also been described.[8]

It has further been found that solutions of sulphonic acids have a power of hydrating acetylene considerably greater than that of solutions of mineral acids of the same acidity. For instance, acetylene may be passed into a mixture of mercuric oxide, *o*-chlorophenolsulphonic acid, and water at 30°–35°, and the aldehyde removed by heating or by means of steam.[9]

Earthenware vessels can be employed if the current of acetylene is so adjusted that the heat produced by the reaction is approximately equal to the heat absorbed by the evaporation of water in the current of gas, and by the cold water added to replace the water consumed in the reaction and that lost by evaporation.[10]

The rapidity of the conversion of acetylene into acetaldehyde by combination with water in the presence of a mercury salt is greatly increased by carrying out the reaction in glacial acetic acid solution at 80°–95°, adding water only as it is required by the reaction. The acetic acid may be partly replaced by ethylidene diacetate.[11]

2. Acetaldehyde is dissolved in glacial acetic acid or a chlorine derivative of acetic acid such as mono-, di-, or trichloroacetic acid and subjected to a stream of air or oxygen at 70°–100°, when it is rapidly converted into acetic acid. A catalyst may be used.[12] It is not necessary to dissolve the aldehyde in acetic acid, for a portion of the aldehyde may be oxidized direct to acetic acid, and then more aldehyde added.[13]

The conversion of acetaldehyde into acetic acid by oxygen is accelerated by the addition of small quantities of manganese compounds—*e.g.*, by dissolving in the acetaldehyde 0·67 % of manganese acetate. The reaction is not explosive, as is the case when compounds of chromium, vanadium, cerium, etc., are used as accelerators.[14]

3. Acetaldehyde is converted almost quantitatively into ethyl acetate by means of small amounts of aluminium alkyl oxides in

[7] Farbw. vorm. Meister, Lucius, und Brüning, U.S. Pats. 1151928 and 1151929 (1915), *J.*, 1915, 1031.

[8] Chem. Fabr. Griesheim-Elektron, Eng. Pat 10140 (1915), *J.*, 1916, 328.

[9] Farbenfabr. vorm. F. Bayer & Co., Fr. Pat. 469497 (1914), *J.*, 1915, 49.

[10] Consort. f. Elektrochem. Ind., Eng. Pat. 16957 (1914), *J.*, 1915, 888.

[11] Consort. f. Elektrochem. Ind., Eng. Pat. 5132 (1915), *J.*, 1916, 556.

[12] Chem. Fabr. Griesheim-Elektron, Eng. Pat. 17424 (1911), *J.*, 1912, 772.

[13] Chem. Fabr. Griesheim-Elektron, Eng. Pat. 8076 (1912), *J.*, 1913, 141.

[14] Consort. f. Elektrochem. Ind., Fr. Pat. 460971 (1913), *J.*, 1914, 42.

presence of catalytic agents such as aluminium chloride, or the product obtained by treating aluminium alkyl oxide with water may be employed.[15] The aluminium alkyl oxide catalyst may be employed in solution, preferably in ethyl acetate.[16] The catalyst is made by adding aluminium chloride during the preparation of the alkyl oxide from aluminium and alcohol.[17]

Instead of increasing the catalytic activity of aluminium alcoholate by treatment with substances containing a halogen, this result may be brought about in other ways; for instance, by pouring the pure chlorine-free molten alcoholate into ethyl acetate.[18]

Another method for the preparation of ethyl acetate is the treatment of acetaldehyde with a filtered solution of aluminium ethoxide in an organic solvent of high boiling point—*e.g.*, nitrobenzene, xylene, or solvent naphtha—at 0°–15°, when a yield of 86 % of the theoretical amount may be obtained with a consumption of about 5 % of aluminium ethoxide.[19] The latter is prepared by the action of anhydrous alcohol on aluminium in the presence of a very small quantity of mercuric chloride. The product is distilled in a vacuum[20] or, with certain precautions, at atmospheric pressure.[21]

4. Acetylene may be converted direct into acetic acid by several processes; for instance, by passing it through a solution of hydrogen peroxide or persulphuric acid in the presence of a mercury compound,[22] or by electrolytic oxidation, using dilute sulphuric acid as electrolyte in the presence of a mercury compound,[23] or by interaction with water and oxygen in the presence of a mercury compound and other contact substances, the reaction being carried out in acetic acid solution. If glacial acetic acid is used, ethylidene diacetate is formed as an intermediate product.[24]

5. When acetic acid is treated with acetylene in the presence of a

[15] Consort. f. Elektrochem. Ind., Eng. Pats. 26825 and 26826 (1913), *J.*, 1914, 666.

[16] Consort. f. Elektrochem. Ind., Ger. Pat. 277188 (1913), addition to 277187, *J.*, 1915, 152; and Ger. Pat. 285990 (1914), addition to 277111, *J.*, 1915, 1167.

[17] Consort f. Elektrochem. Ind., Ger. Pat. 286182 (1914), addition to 277111, *J.*, 1916, 72.

[18] Consort. f. Elektrochem. Ind., Eng. Pat. 4887 (1915), *J.*, 1916, 653.

[19] Farbw. vorm. Meister, Lucius, und Brüning, Eng. Pat. 1288 (1915), *J.*, 1916, 141.

[20] Farbw. vorm. Meister, Lucius, und Brüning, Ger. Pat. 286596 (1913), *J.*, 1915, 1168.

[21] Farbw. vorm. Meister, Lucius, und Brüning, Ger. Pat. 289157 (1914), *J.*, 1916, 385.

[22] Farbenfabr. vorm. F. Bayer & Co., Fr. Pat. 467515 (1914), *J.*, 1914, 83[illegible].

[23] Farbenfabr. vorm. F. Bayer & Co., Fr. Pat. 467778 (1914), *J.*, 1914, 830.

[24] Chem. Fabr. Griesheim-Elektron, Fr. Pat. 473158 (1914), *J.*, 1915, 491.

mercury salt, acetic anhydride and ethylidene diacetate are formed. On distillation the mixture can be separated into acetic anhydride and acetaldehyde.[25] The mercuric sulphate which is employed as a catalyst is best made by dissolving mercuric oxide in the acetic acid to be used, and then adding the necessary quantity of sulphuric acid.[26] Another method of preparing acetic anhydride from ethylidene diacetate consists in passing the vapour of the latter through a tube charged with pumice stone at 250° to 300°, when the condensed product contains 25·3 % acetaldehyde, 17·1 % acetic acid, 49 % acetic anhydride, and 7 % unchanged ethylidene diacetate.[27]

Effect of the War on Synthetic Drugs.

Before the war a large number of drugs and fine chemicals were manufactured almost exclusively in Germany, and after the outbreak of war many substances became increasingly scarce and consequently costly. This is well shown in the case of derivatives of salicylic acid and some other synthetic drugs as follows[28] :—

—		Prices immediately before the war.	Prices on Jan. 1, 1915.	Prices on Jan. 1, 1916.
Acetanilide	per lb.	10*d.*	2*s.*	6*s.* 9*d.* to 7*s.*
Acetylsalicylic acid	,,	2*s.*	6*s.* 6*d.*	48*s.* to 50*s.*
Hexamine	,,	1*s.* 10*d.*	3*s.* 6*d.*	5*s.* 6*d.*
Phenacetin	,,	2*s.* 9*d.*	6*s.* 6*d.*	60*s.*
Phenazone	,,	6*s.* 6*d.*	9*s.* 6*d.*	75*s.*
Salol	,,	1*s.* 10*d.*	4*s.* 9*d.*	47*s.*
Salicylic acid ...	,,	1*s.*	5*s.*	20*s.*
Sodium salicylate ...	,,	1*s.* 3*d.*	5*s.*	22*s.*

The urgent demand for these and other drugs has created a supply both from home and from neutral countries, in particular Switzerland and the United States of America. As regards home production, the *British and Colonial Druggist* stated in its issue of February 26, 1915,[29] that there was evidence that British firms were producing large or small quantities of the following: acetanilide, acetylsalicylic acid, amidol, anethol, benzaldehyde, citral, citronellol, cocaine, β-eucaine, eugenol, formaldehyde, hexamine, methyl sulphonal, phenacetin, quinol, salicylic acid, salvarsan, sodium salicylate, sulphonal, terpineol, thymol, triacetin, and vanillin.

[25] G. Boiteau, Fr. Pat. 474828 (1913), *J.*, 1915, 1116.
[26] G. Boiteau, Fr. Pat. 475853 (1914), *J.*, 1916, 72.
[27] Bosnische Electricitäts-A.-G., Eng. Pat. 23190 (1914), *J.*, 1915, 982.
[28] *Pharm. J.*, 1916, **96**, 6. [29] *J.*, 1915, 302.

Evidence is furnished by the price records that many of these drugs are becoming less scarce. Thus in July, 1916, salicylic acid and sodium salicylate were obtainable at 15*s.* 6*d.* per lb., acetylsalicylic acid at 47*s.* per lb., and hexamine at 4*s.* 9*d.* per lb.[30] Phenacetin, however, is scarcer at 85*s.* to 90*s.* per lb.[31] A further fall in the prices of many drugs has taken place during the last half-year, and the following are the prices of those listed in the above table at the beginning of the present year:—

		Prices on Jan. 1st, 1917.	
		s.	*d.*
Acetanilide	(per lb.)	2	10
Acetylsalicylic acid	,,	18	6
Hexamine	,,	2	9
Phenacetin	,,	92	6
Phenazone	,,	33	0
Salol	,,	10	6
Salicylic acid	,,	4	9
Sodium salicylate	,,	5	9

Several synthetic drugs have been prepared in small quantities in the chemical departments of our Universities and Technical Colleges. J. F. Thorpe,[32] for instance, records the preparation at the Imperial College of Science and Technology of 30 lb. of phenacetin, 50 lb. of hexamine, and 1½ lb. of β-eucaine, and mentions the methods employed.

Phenacetin was prepared according to the following scheme:—

	Aniline	$C_6H_5\cdot NH_2$
Acetylation →	Acetanilide	$C_6H_5\cdot NH\cdot CO\cdot CH_3$
Nitration →	*p*-Nitroacetanilide	$NO_2\cdot C_6H_4\cdot NH\cdot CO\cdot CH_3$
Alkali →	Na salt of *p*-Nitrophenol	$NO_2\cdot C_6H_4\cdot ONa$
C_2H_5Br →	*p*-Nitrophenetole	$NO_2\cdot C_6H_4\cdot OEt$
Reduction →	*p*-Phenetidine	$NH_2\cdot C_6H_4\cdot OEt$
Acetylation →	Phenacetin	$CH_3\cdot CO\cdot NH\cdot C_6H_4\cdot OEt$

Difficulties arose in the reduction of *p*-nitrophenetole to *p*-phenetidine, the use of tin and strong hydrochloric acid yielding an impure product contaminated with chloro-*p*-phenetidine, but these were overcome by the employment of dilute acid.[33] The preparation of one of the intermediate

[30] *Pharm. J.*, 1916, July 1, **97**, 16.

[31] *Pharm. J.*, 1916, July 8, **97**, 42.

[32] *Nature*, Jan. 28, 1915, p. 593; *J.*, 1915, 150.

[33] Miss W. G. Hurst and J. F. Thorpe, *Chem. Soc. Trans.*, 1915, **107**, 934; *J.*, 1915, 863.

products mentioned above, ethyl bromide, has been the subject of study, and two authors[34] agree that yields in the neighbourhood of 90 per cent. of the theoretical are readily obtainable by slow distillation of a not too concentrated alcohol-water-sulphuric acid mixture with potassium bromide.

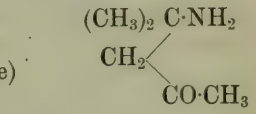
In the same connection a recent patent[35] may be noted, according to which methyl and ethyl halides may be obtained in good yield by heating methyl or ethyl alcohol with an aqueous solution of a hydrohalogen acid and the corresponding calcium halide in an open vessel at a temperature not exceeding 100°.

The method recorded by Thorpe for the preparation of β-eucaine is indicated by the following scheme :—

Acetone $CH_3{\cdot}CO{\cdot}CH_3$

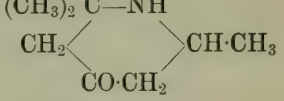
Ammonia and oxalic acid →

Diacetoneamine (hydrogen oxalate)



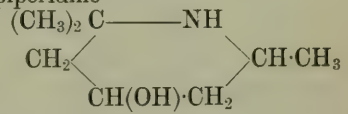
Condensation with paraldehyde →

Vinyldiacetoneamine (oxalate)



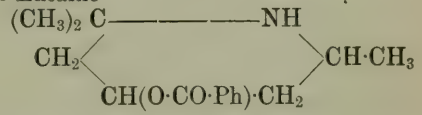
Reduction and isomerisation →

Cis form of the hydroxypiperidine



Benzoyl chloride →

β-Eucaine



Other drugs besides the three mentioned by Thorpe have also been prepared on the laboratory scale—for instance, novocaine, the hydrochloride of diethylaminoethyl *p*-aminobenzoate ($NH_2{\cdot}C_6H_4{\cdot}CO{\cdot}O{\cdot}CH_2{\cdot}CH_2{\cdot}NEt_2$, HCl).

Methods have been worked out for the preparation of ethylene chlorohydrin and diethylamine, which are required for the preparation

[34] F. E. Weston, *Chem. Soc. Trans.*, 1915, **107**, 1489; *J.*, 1915, 1165. A. Holt, *Chem. Soc. Trans.*, 1916, **109**, 1; *J.*, 1916, 275.

[35] Actienges. für Anilinfabr., Ger. Pat. 280740 (1913), *J.*, 1915, 575.

of diethylaminoethyl alcohol, an intermediate product in the manufacture of novocaine, and two publications on the preparation of diethylamine have appeared. In the more important process[36] the reaction between *p*-nitrosodiethylaniline and sodium hydroxide is employed :—

$$NO{\cdot}C_6H_4{\cdot}NEt_2 + NaOH = NHEt_2 + NO{\cdot}C_6H_4{\cdot}ONa$$

and the details of manipulation are so well worked out that 1 kilogram per day can readily be made on the laboratory scale, the yield being 86·5 % of the theoretical and the product of constant boiling-point 56°. The second method of preparation[37] depends on the interaction of ethyl bromide and ammonia, when a mixture of mono-, di-, and tri-ethylamines was obtained. These were separated by fractional distillation, and the mono-ethylamine was ethylated again, when a further quantity of diethylamine resulted. The total yield of the latter does not appear to have been more than 23 % of the theoretical. The methods of preparing acetic anhydride—an important intermediate product in synthetic work—have been fully reviewed by J. T. Hewitt and C. H. Lumsden,[38] whose article should be consulted. They conclude that the chlorides of phosphorus and sulphur are the most suitable reagents for use in the preparation of this substance. In the discussion following their paper C. F. Cross referred to the possibility of producing acetic anhydride from acetylene. The processes for this purpose are reviewed above (pp. 274–5), together with other applications of acetylene to synthetic purposes.

In connection with the heavier synthetic drugs it may be mentioned that *The Chemist and Druggist* has published methods for manufacturing the following, together with references to the literature in each case: salicylic acid, acetylsalicylic acid, salol,[39] antipyrine,[40] chloral, and paraldehyde.[41] For the preparation of acetanilide a method has been published by which aniline and acetic acid are gently boiled together with 2–3 % of zinc chloride.[42]

As regards proprietary names of medicinal substances, the trade marks of alien enemies have been avoided in several cases, either generally or on behalf of specified manufacturers. Cases in point are aspirin, lysol, salvarsan,[43] and urotropine.[44] A useful index list of trade

[36] T. Slater Price, S. A. Brazier, and A. S. Wood, *J.*, 1916, 147.
[37] W. E. Garner and D. Tyrer, *Chem. Soc. Trans.*, 1916, **109**, 174; *J.* 1916, 382.
[38] *J.*, 1916, 210.
[39] *Chem. and Drug.*, 1914, **85**, 313; *J.*, 1914, 886.
[40] *Ibid.*, 273; *J.*, 1914, 887.
[41] *Ibid.*, 336; *J.*, 1914, 941.
[42] Häussermann, *J. Pharm. Chim.*, 1914, **10**, 375; *J.*, 1914, 1223.
[43] *J.*, 1914, 1028.
[44] *J.*, 1915, 512.

names of synthetic drugs is given in the Journal,[45] whilst *The Chemist and Druggist* has given an index list of pharmaceutical products bearing trade names of which the patents have expired.[46]

Salicylic Acid and its Derivatives.

Reference has already been made to the price of salicylates in the previous article. It appears that there are now about a dozen firms engaged in the manufacture of salicylates in this country, and the position of the industry has been discussed.[47] Natural salicylates are to be manufactured in India from the leaves of *Gaultheria fragrantissima*,[48] whilst the synthetic preparation of salicylic aldehyde in this country is also proposed.[49]

The cause of the coloration developed in a solution of sodium salicylate to which sodium bicarbonate has been added was studied by H. G. Greenish and A. E. Beesley,[50] who have shown that the coloration is much less when sodium hydroxide or carbonate is substituted for the bicarbonate, and is most marked when sodium sesquicarbonate ($Na_2CO_3,NaHCO_3$) is employed. Small amounts of certain reducing agents—for instance, sulphites—greatly inhibit development of this coloration. In a contribution to the same subject W. Macadie[51] attributes the discoloration of sodium salicylate solution to the presence of traces of free ammonia in the air, and states that the solution remains colourless if certain precautions to prevent the access of ammonia are taken. It is possible that the coloration recorded by the previous authors is due to the presence of traces of ammonia in the alkali employed.

H. L. Smith[52] states that pure salicylic acid, dried in a vacuum over sulphuric acid, melts at 158·5°, whilst the presence of 1 % of *p*-hydroxybenzoic acid lowers the melting-point to 155°–156°. The melting-point required by the British Pharmacopœia is 156°–157°. The author describes a test for the presence of *p*-hydroxybenzoic acid in salicylic acid sensitive to less than 1 %, and based on the greater solubility of the calcium salt of the *para*-acid in water. A new colour reaction for salicylic acid, which serves to distinguish it from other phenolic substances, is described by P. A. W. Self.[53]

[45] *J.*, 1914, 1028.
[46] *Chem. and Drug.*, various dates during 1915; *J.*, 1915, 301, 635, 922.
[47] *Ibid.*, Aug. 26, 1916, 908.
[48] *Perf. and Essent. Oil Rec.*, May, 1916; *J.*, 1916, 652.
[49] *Chem. and Drug.*, Sept. 2, 1916, 925.
[50] *Pharm. J.*, 1915, **94**, 201; *J.*, 1915, 247.
[51] *Pharm. J.*, 1915, **94**, 355; *J.*, 1915, 377.
[52] *Analyst*, 1916, **41**, 3; *J.*, 1916, 196.
[53] *Pharm. J.*, 1915, **94**, 521; *J.*, 1915, 511.

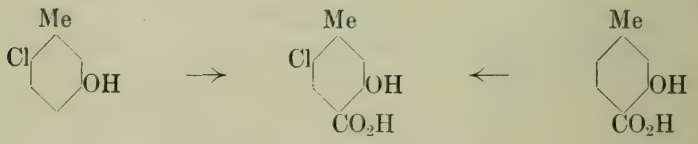
The decomposition of acetylsalicylic acid by water has been studied by several authors,[54] but the results obtained are somewhat indecisive, and do not readily lend themselves to summarization.

A number of patents are concerned with the preparation of metallic salts of acetylsalicylic acid, such as the sodium, lithium, and magnesium salts. The preparation of the bismuth salt[55] has also been described, and the manufacture of the urea[56] and α-bromo*iso*valerylurea[57] salts protected.

Acetylsalicylic acid chloride, which had previously been prepared by the action of phosphorus pentachloride on acetylsalicylic acid in the presence of dimethylaniline,[58] can also be made by heating the acid with thionyl chloride in benzene.[59] It is a convenient reagent for the preparation of esters of acetylsalicylic acid, such as the 8-hydroxyquinoline ester,[60] or substituted acid amides, such as the N-acetylsalicylyl derivative of theobromine.[61]

Amongst the new acyl derivatives of salicylic acid, acetylglycollylsalicylic acid, $CO_2H{\cdot}C_6H_4{\cdot}O{\cdot}CO{\cdot}CH_2{\cdot}O{\cdot}CO{\cdot}CH_3$, may be mentioned,[62] and attention may also be drawn to the claim that the acyl derivatives of C-allyl-*o*-hydroxybenzoic acids[63] have more pronounced antipyretic, antineuralgic and antirheumatic properties than the acylsalicylic acids.

6-Chloro-1-methyl-3-hydroxybenzene-4-carboxylic acid is stated to have powerful antiseptic properties, and to be 2-4 times less toxic than salicylic acid, whereas the cresotic acids are more toxic than this. It may be prepared either by the action of carbon dioxide under pressure at 160° to 180° on *p*-chloro-*m*-cresol-sodium[64] or by chlorination of m-cresotic acid.[65]



[54] D. E. Tsakalotos and S. Horsch, *Bull. Soc. Chim.*, 1914, **15**, 743; 1915, **17**, 186, 401; *J.*, 1915, 101, 733; 1916, 140. H. L. Smith, *Pharm. J.*, 1915, **94**, 200; *J.*, 1915, 247. E. J. Parry, *Chem. and Drug.*, 1916, 611.

[55] L. Vanino and F. Mussgung, *Arch. Pharm.*, 1915, **253**, 511; *J.*, 1916, 556.

[56] Dr. Schütz & Co., Ger. Pat. 274046 (1913), *J.*, 1914, 806.

[57] Knoll & Co., Ger. Pat. 274349 (1912), *J.*, 1914, 806.

[58] Farbenfabr. vorm. F. Bayer & Co., Ger. Pats. 201325, 201326.

[59] R. Wolffenstein, Ger. Pat. 277659 (1911), *J.*, 1915, 303.

[60] R. Wolffenstein, Ger. Pat. 281007 (1913), *J.*, 1915, 452.

[61] E. Merck, Ger. Pat. 290205 (1913), *J.*, 1916, 557.

[62] W. Hiemenz, U.S. Pat. 1122201 (1914), *J.*, 1915, 451.

[63] Farbenfabr. vorm. F. Bayer & Co., Ger. Pat. 274047 (1913), *J.*, 1914, 806.

[64] J. D. Riedel A.-G., Ger. Pat. 275093 (1913), *J.*, 1914, 807.

[65] J. D. Riedel A.-G., Fr. Pat. 468949 (1914), *J.*, 1914, 984.

Glycerophosphates.

In the preparation of sodium glycerophosphate by Poulenc's method[66] a crystalline salt is obtained together with an uncrystallizable mother liquor still rich in sodium glycerophosphate. The constitution of the crystalline salt has been a matter of some controversy,[67] but has now been definitely established.

When α-dichlorohydrin (I) is combined with phosphoryl chloride, and the reaction product hydrolysed by milk of lime, a crystalline calcium salt (II) is produced, which on boiling with aqueous sodium carbonate yields glycerol and sodium β-glycerophosphate (III).

$$\begin{array}{l} CH_2Cl \\ | \\ CH{-}OH \\ | \\ CH_2Cl \end{array} + POCl_3 \longrightarrow \begin{array}{l} CH_2Cl \\ | \\ CH{\cdot}O{-}P{-}O{\cdot}CH \\ | \quad | \quad | \\ CH_2Cl \ OCa \ CH_2Cl \end{array} \longrightarrow \begin{array}{l} CH_2{\cdot}OH \\ | \\ CH{\cdot}O{\cdot}PO(ONa)_2 \\ | \\ CH_2{\cdot}OH \end{array} + \begin{array}{l} CH_2{\cdot}OH \\ | \\ CH{\cdot}OH \\ | \\ CH_2{\cdot}OH \end{array}$$

I. II. III.

This is identical with Poulenc's salt, the constitution of which is thus established synthetically.[68] The same conclusion has been arrived at by an analytical method based on the following argument: α-glycerophosphoric acid, $(HO)_2PO{\cdot}O{\cdot}CH_2{\cdot}CH(OH){\cdot}CH_2OH$, should be capable of oxidation to a derivative of dihydroxyacetone, $(HO)_2PO{\cdot}O{\cdot}CH_2{\cdot}CO{\cdot}CH_2OH$, which could then be recognized by Denigès' reactions, whereas the β-acid should not. Experiments showed that Poulenc's crystalline salt when examined in this way gave a negative result, whereas the uncrystallizable liquor gave a positive result, thus indicating that the crystalline salt is the β-salt, whilst the uncrystallizable liquor contains an appreciable amount of the α-salt.[69]

The salts of α-glycerophosphoric acid have now been prepared synthetically by two methods. The first method employed was the action of trisodium phosphate on α-monochlorohydrin, and the reaction was represented by King and Pyman[70] as follows:—

$$CH_2(OH){\cdot}CH(OH){\cdot}CH_2Cl + (NaO)_3PO = CH_2(OH){\cdot}CH(OH){\cdot}CH_2{\cdot}O{\cdot}PO(ONa)_2 + NaCl.$$

Later, however, O. Bailly[71] showed that the course of the reaction was less simple than is indicated by the above equation, and that

[66] Fr. Pat. 373112 (1906), *J.*, 1907, 716.

[67] V. Paolini, *Atti R. Accad. Lincei*, 1911 (V), **20**, i, 807; 1912, **21**, ii, 350; *Gazzetta*, 1912, **42**, i, 57; *J.*, 1912, 203, 1053. P. Carré, *Compt. rend.*, 1912, **154**, 220; *J.*, 1912, 203.

[68] H. King and F. L. Pyman, *Chem. Soc. Trans.*, 1914, **105**, 1238; *J.*, 1914, 665.

[69] L. Grimbert and O. Bailly, *Compt. rend.*, 1915, **160**, 207; *J.*, 1915, 247.

[70] *Loc. cit.* [71] *Compt. rend.*, 1915, **161**, 677; *J.*, 1916, 70.

glycide is probably produced as an intermediate product, which then combines with sodium phosphate to give sodium α-glycerophosphate as follows:—

$$CH_2(OH)\cdot CH(OH)\cdot CH_2Cl + (NaO)_3PO$$
$$= CH_2(OH)\cdot CH\!-\!CH_2 + (NaO)_2PO(OH) + NaCl$$
$$\qquad\qquad\qquad\qquad\quad \backslash O /$$

$$CH_2(OH)\cdot CH\cdot CH_2 + (NaO)_2PO(OH)$$
$$\quad\backslash O /$$
$$= CH_2(OH)\cdot CH(OH)\cdot CH_2\cdot O\cdot PO(ONa)_2.$$

In confirmation of this view he was able to synthesize sodium α-glycerophosphate by the action of glycide on sodium phosphate.

The same author has also synthesized the salts of α-glycerophosphoric acid by an entirely novel method, the oxidation of sodium mono-allyl phosphate by means of potassium permanganate.[72]

$$CH_2{:}CH\cdot CH_2\cdot O\cdot PO(ONa)_2 \longrightarrow CH_2(OH)\cdot CH(OH)\cdot O\cdot PO(ONa)_2.$$

As regards the glycerophosphoric acid of egg-lecithin, O. Bailly[73] adheres to the view of former workers that this is a mixture. More recently, however, H. Maclean[74] has shown that "lecithin" itself is a mixture in variable proportions of two somewhat similar substances, true lecithin and kephalin, and remarks that possibly the true lecithin part of "lecithin" may have one form of this acid, while the kephalin part may have the other form. In conclusion, reference may be made to a paper by J. C. Umney and C. T. Bennett[75] on the composition of the glycerophosphates of commerce.

Hypnotics.

Little progress has been made in the discovery of new hypnotics, and the results recorded in the literature deal chiefly with variations on well-known themes. Further methods of preparing "adalin," diethylbromoacetylurea, $Et_2CBr\cdot CO\cdot NH\cdot CO\cdot NH_2$, have been described,[76] in addition to those already known, whilst its acyl-derivatives, $Et_2CBr\cdot CO\cdot NH\cdot CO\cdot NH\cdot CO\cdot R$, have also been protected.[77] α-Bromo*iso*valerylurea, $Me_2CH\cdot CHBr\cdot CO\cdot NH\cdot CO\cdot NH_2$ is a compound of the same type.[78]

[72] *Compt. rend.*, 1915, **160**, 663; *J.*, 1915, 634.
[73] *Ibid.*, 1915, **160**, 395; *J.*, 1915, 511.
[74] *Biochem. J.*, 1915, **9**, 351; *J.*, 1915, 1114.
[75] *Yearbk. Pharm.*, 1914, 491; *J.*, 1914, 844.
[76] Farbenfabr. vorm. F. Bayer & Co., third addition (1914) to Fr. Pat. 417803 (1910), *J.*, 1915, 512.
[77] Farbenfabr. vorm. F. Bayer & Co., Ger. Pat. 286760 (1913), *J.*, 1916, 197.
[78] Knoll & Co., Ger. Pat. 275200 (1912), *J.*, 1914, 806.

Attempts to improve on veronal continue; thus, the alkyl-alkyloxyalkyl- or di-alkyloxyalkyl-barbituric acids, such as the di-ethoxyethyl derivative, $(C_2H_5{\cdot}O{\cdot}C_2H_4)_2C<\begin{matrix}CO{\cdot}NH\\CO{\cdot}NH\end{matrix}>CO$, are claimed to be less toxic than veronal.[79]

Further work has been carried out on the compounds of CC-dialkyl-barbituric acids with alkaloids: the compound of quinine and veronal, known as "chineonal," was stated to have a more powerful hypnotic effect than veronal itself,[80] and it has now been found that this effect is again enhanced by substituting for quinine certain of its derivatives; moreover, the products are much less toxic than "chineonal," thus, propylhydrocupreine-dipropylbarbituric acid is practically non-poisonous.[81]

An interesting study[82] has been carried out of the effect produced on the physiological properties of trichlorobutyl alcohol, "chloretone," $Me_2C(OH)CCl_3$, by esterification with different acids. The results show that the esters are not as a rule hydrolysed in the organism, and that they frequently exert an action, *e.g.*, tetanic, which is not shared by the parent alcohol. The hypnotic properties, which are well marked in the latter, diminish in the acetate, whilst the toxicity increases. Further, in the homologous series rising from the acetate to the *iso*valerate, the highest member tested, a progressive fall in the hypnotic properties and an increase in the toxicity is noted. The mono- and tri-chloro-acetates are both less toxic and less narcotic than the acetate, whilst the pyruvate is highly toxic and has no hypnotic properties. An interesting case is presented by the allophanate, which is not hypnotic, although the conversion of an alcohol into its allophanate is attended in many other cases by a considerable enhancement of the narcotic power of the alcohol. Trichlorobutyl-dimethylaminoacetate is markedly hypnotic, and still more so the diethylaminoacetate, but the diethylamino*iso*valerate is not. The malonate, cinnamate, and dibromocinnamate were also devoid of narcotic properties. The acid malonic ester of trichlorobutyl alcohol has the same analgesic properties as the original alcohol without the anæsthetic properties of the latter.[83]

Organic Arsenic Compounds.

The earlier literature dealing with the developments of this work up to the preparation of "salvarsan" and "neosalvarsan" has already been

[79] Chem. Werke vorm. H. Byk, Ger. Pat. 285636 (1912), *J.*, 1915, 1167.

[80] E. Merck, Ger. Pat. 249908 (1911), *J.*, 1912, 952.

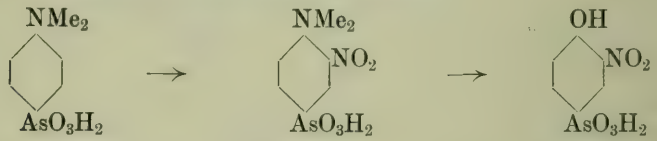
[81] E. Merck, Ger. Pat. 291421 (1914), *J.*, 1916, 654.

[82] R. Wolffenstein, A. Loewy, and M. Bachstez, *Ber.*, 1915, **48**, 2035; *J.*, 1916, 328.

[83] R. Wolffenstein, Ger. Pat. 289001 (1913), *J.*, 1916, 437.

the subject of several reviews.[84] It will, therefore, be sufficient to describe here the newer preparations and some variants in the methods of manufacture of the older substances. Since the commencement of the war, licences to work patents for the manufacture of "salvarsan" and "neosalvarsan" have been granted to a British firm[85] who supply these products under the trade names of "kharsivan" and "neokharsivan," and to a French firm whose corresponding products are called "arsenobenzol" and "novarsenobenzol." The latter firm have protected some new methods in this field, which may be mentioned.

Dimethylaniline combines with arsenic trichloride in the presence of pyridine, and the product yields *p*-dimethylaminophenylarsinic acid (I) on oxidation.[86] This can be nitrated to yield 3-nitro-4-dimethylaminophenylarsinic acid (II), from which 3-nitro-4-hydroxyphenylarsinic acid (III) is obtained by the action of alkali.[87]



I. II. III.

A new method is also described for the reduction of the latter to "salvarsan." It has been known for some years[88] that the reduction of this acid with zinc and hydrochloric acid led to the ultimate reduction-product 3-amino-4-hydroxyphenylarsine, $(NH_2)(OH)C_6H_3{\cdot}AsH_2$, a stage beyond "salvarsan," but it has now been found that the addition of sulphurous acid prevents the reduction from proceeding past the desired arseno-stage.[89]

An earlier method for the preparation of 3-nitro-4-hydroxyphenylarsinic acid was the nitration of *p*-hydroxyphenylarsinic acid. This may be obtained by the action of arsenic acid on phenol at a high temperature, but the product is thus obtained in a very crude state. It is now claimed[90] that it is readily purified by crystallization of its sodium salt.

Several new compounds allied to "salvarsan" have recently been brought into use. "Sodium salvarsan" is prepared by precipitating a

[84] W. H. Martindale, *J.*, 1909, 907. G. T. Morgan, *Pharm. J.*, 1914, **92**, 537, 567. A. A. Boon, *Pharm. J.*, 1914, **93**, 836; *J.*, 1914, 1187; *Chem. Soc. Ann. Reports*, 1911, 117; 1915, 124.

[85] *J.*, 1914, 1028.

[86] Poulenc Frères and K. Oechslin, Fr. Pat. 473704 (1913), *J.*, 1915, 734.

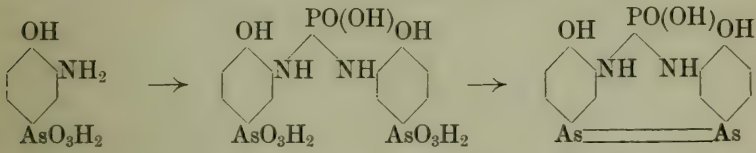
[87] Poulenc Frères, Eng. Pat. 22521 (1914), *J.*, 1916, 437.

[88] Farbw. vorm. Meister, Lucius, und Brüning, Eng. Pat. 11625 (1911), *J.*, 1912, 605.

[89] Poulenc Frères, Eng. Pat. 21421 (1914), *J.*, 1915, 1225.

[90] F. W. Kay, Eng. Pat. 6322 (1915), *J.*, 1916, 437.

solution of "salvarsan" in aqueous sodium hydroxide with alcohol in the presence of a substance capable of stabilizing the product; this may be sodium hydrosulphite or sodium formaldehyde-sulphoxylate,[91] mannitol or other polyhydric alcohol containing more than three hydroxyl groups.[92] "Sodium salvarsan" is said to have proved satisfactory in the ambulatory treatment of syphilis.[93] "Copper salvarsan" is stated to be useful in sleeping-sickness; it is prepared by mixing salvarsan with a copper salt, adding sodium hydroxide, and precipitating the mixture.[94] A compound of "salvarsan" with silver bromide and antimony is known as "luargol," or "preparation 102." It is stated[95] to have the composition $(C_{12}H_{12}O_2N_2As_2)_2,AgBr,SbO(H_2SO_4)_2$, and favourable reports on its stability and clinical value have appeared.[96] Another derivative of "salvarsan," which has recently come into prominence, bears the trade name of "galyl." This compound appears to be prepared by the action of phosphorus oxychloride on 3-amino-4-hydroxyphenylarsinic acid in the presence of aqueous sodium hydroxide, and subsequent reduction of the product by sodium hydrosulphite.[97]



The aminohydroxyphenylarsinic acid required may be obtained by the electrolytic reduction of 3-nitro-4-hydroxyphenylarsinic acid.[98]

At this point reference may be made to two substances, "intramine" and "ferrivine," although they do not contain arsenic, since they have recently been introduced for the treatment of syphilis. "Intramine" is di-*o*-aminophenyl disulphide, $NH_2{\cdot}C_6H_4{\cdot}S{\cdot}S{\cdot}C_6H_4{\cdot}NH_2$; its therapeutic effect was better than that of the di-*para* isomeride, whilst two of its

[91] Farbw. vorm. Meister, Lucius, und Brüning, Eng. Pat. 15931 (1912), *J.*, 1913, 161.

[92] Farbw. vorm. Meister, Lucius, und Brüning, Eng. Pat. 24152 (1914), *J.*, 1915, 1165.

[93] Wechselmann, *Münch. Med. Wochenschr.*, 1915, 177; Dreyfus, *ibid.*, 178.

[94] Farbw. vorm. Meister, Lucius, und Brüning, Eng. Pat. 1247 (1914), *J.*, 1914, 942.

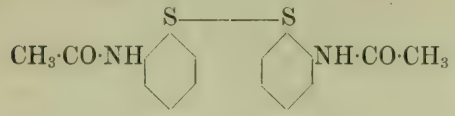
[95] J. Danysz, *Compt. rend.*, 1914, **159**, 452; *J.*, 1914, 942.

[96] A. Renault, L. Fournier, and L. Guénot, *Compt. rend.*, 1915, **161**, 685; Dalimier and Lévy-Franchel, *ibid.*, 1916, **162**, 440; from *Pharm. J.*, 1916, **96**, 77, 423.

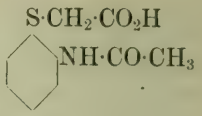
[97] A. Mouneyrat, Eng. Pat. 9234 (1915), *J.*, 1916, 72.

[98] A. Mouneyrat, Eng. Pat. 3087 (1915), *J.*, 1916, 437.

derivatives, di-*o*-acetylaminophenyl disulphide (I), and *o*-acetylaminophenylthioglycollic acid (II)



I.



II.

had practically no therapeutic action.[99] "Ferrivine" is ferric sulphanilate, $Fe(SO_3 \cdot C_6H_4 \cdot NH_2)_3$.[100]

Alkaloids.

In dealing with alkaloids generally, it is proposed to review briefly certain lines of work which have been prominent recently, namely, reduction by catalytic methods and demethylation of alkaloids.

Reduction.—Many patents have been taken out during the last few years covering the reduction of alkaloids by means of hydrogen in the presence of a catalyst. This mode of reduction in its application to organic substances generally was reviewed by A. W. Crossley in a lecture to the Pharmaceutical Society,[101] and the reduction of strychnine and brucine was referred to. The reduction of the cinchona alkaloids by hydrogen in the presence of various catalysts has been the subject of several patents,[102] and is utilized in the preparation of the medicinal substance "optoquin," which is ethyldihydrocupreine. Morphine and codeine yield dihydro-derivatives under similar conditions,[103] whilst dihydrocodeine may also be prepared by the methylation of dihydromorphine.[104] The latter substance can be obtained not only by hydrogenating pure morphine, but also from the mixture produced by hydrogenating opium.[105] Colchicine also yields a reduction product by this method.[106] An alternative method for the reduction of quinine to hydroquinine, and morphine to dihydromorphine, is the treatment of the alkaloid with formic acid and a finely divided metal of

[99] J. E. R. McDonagh, *Lancet*, 1916, **190**, 238.

[100] J. E. R. McDonagh, *ibid.*, 1916, **190**, 1030.

[101] *Pharm. J.*, 1914, **92**, 604, 637, 676; *J.*, 1914, 1135.

[102] Verein. Chininfabr. Zimmer & Co., U.S. Pat. 989664 (1911); Eng. Pat. 3948 (1912); Eng. Pat. 27952 (1911); Ger. Pat. 254712 (1911), *J.*, 1911, 649; 1912, 604, 843; 1913, 213. A. Skita, Eng. Pat. 16283 (1913), *J.*, 1913, 989. C. F. Boehringer und Soehne, Eng. Pats. 21883 and 21948 (1914), *J.*, 1915, 1225.

[103] H. and B. Oldenburg, Ger. Pat. 260233 (1911), *J.*, 1913, 711. C. F. Boehringer und Soehne, *loc. cit.*

[104] Knoll & Co., Ger. Pat. 278111 (1913), *J.*, 1915, 249.

[105] F. Hoffmann-La Roche & Co., Ger. Pat. 278107 (1913), *J.*, 1915, 249.

[106] F. Hoffmann-La Roche & Co., Ger. Pat. 279999 (1913), *J.*, 1915, 452.

the platinum group, the reduction taking place with liberation of carbon dioxide.[107]

Demethylation.—Whilst a large number of the naturally-occurring alkaloids contain an N-methyl (:N·CH$_3$) group, the corresponding imino-bases, containing the group :NH in the place of :N·CH$_3$ are in many cases unknown. In a few cases where the alkaloids themselves are sufficiently resistant, the N-methyl group can be converted into the imino-group by oxidation; for instance, tropine yields nortropine on oxidation with potassium permanganate. This method, however, has only a limited scope, and the newer methods of effecting this result without attacking the molecule at other points are therefore of importance. O. Diels and E. Fischer[108] state that methylpiperidine, atropine, morphine, and codeine can be demethylated by the addition of methyl azodicarboxylate and subsequent hydrolysis of the addition product by hydrochloric acid. The general reaction may be expressed as follows:—

$$\begin{array}{l} R{:}N{\cdot}CH_3 + N{\cdot}CO_2Me \\ \qquad\qquad\quad \| \\ \qquad\qquad\quad N{\cdot}CO_2Me \end{array} \longrightarrow \begin{array}{l} R{:}N{\cdot}CH_2{\cdot}N{\cdot}CO_2Me \\ \qquad\qquad\quad | \\ \qquad\qquad\quad NH{\cdot}CO_2Me \end{array} + H_2O \longrightarrow$$

$$R{:}NH + \begin{array}{l} NH{\cdot}CO_2Me \\ | \\ NH{\cdot}CO_2Me \end{array} + H{\cdot}CHO$$

The second method, due to J. von Braun,[109] has been successfully applied to morphine and codeine. Here the acetylated alkaloid is treated with cyanogen bromide, when the methyl group attached to the nitrogen atom is replaced by the cyano-group (:N·CH$_3$ → :N·CN), and subsequent hydrolysis first removes the acetyl groups and then replaces the cyano-group on the nitrogen atom by a hydrogen atom, yielding normorphine or norcodeine. The preparation of these demethylated alkaloids is of importance, for they can be readily converted into homologues of the original alkaloid by replacing the imino-hydrogen atom by alkyl-groups. The homologues thus prepared will differ from the originals in their physiological properties, and the study of the homologues of morphine and codeine has been begun by von Braun. The latter's method for the preparation of normorphine and norcodeine has been protected by patent,[110] and a modified process is also described[111] in which cyanogen chloride is used instead of the bromide. It is claimed that the

[107] Verein. Chininfabr. Zimmer & Co., Eng. Pat., 10204 (1913), 14247 (1913), *J.*, 1913, 989; 1914, 844.

[108] *Ber.*, 1914, **47**, 2043; *J.*, 1914, 765.

[109] *Ber.*, 1914, **47**, 2312; *J.*, 1914, 843.

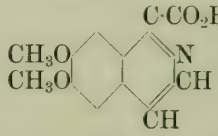
[110] F. Hoffmann-La Roche & Co., Ger. Pat. 286743 (1914), *J.*, 1916, 197.

[111] F. Hoffmann-La Roche & Co., Ger. Pat. 289273 (1915), *J.*, 1916, 438.

N-allyl derivatives prepared by introducing the allyl-group into norcodeine and dihydronorcodeine are energetic antidotes to morphine.[112]

In dealing with individual alkaloids, it may be observed that hitherto our knowledge of the chemical constitutions of several of those employed medicinally has been very scanty. Recently, however, progress has been made with certain members of this class, namely, emetine, eserine, hyoscine, and yohimbine.

Emetine.—This alkaloid has been much used for the cure of amœbic dysentery in the Expeditionary Forces operating in hot climates, and considerable experience has been gained with regard to its medicinal properties. It can be given in comparatively large doses, but may give rise to toxic symptoms if given indiscriminately, and several writers have drawn attention to this point.[113] It may be noted that different commercial samples of emetine salts vary in their toxicity,[114] and some can be shown to contain cephaeline,[115] which is known to be more toxic than emetine. Emetine is usually administered intramuscularly as the hydrochloride, but recently oral treatment with the double iodide of emetine and bismuth has been introduced, more especially for the cure of cyst-carriers.[116] As regards the chemical constitution of the alkaloids of ipecacuanha, some advances have been made, two long papers on the subject having appeared in 1914. Both agree that cephaeline has the formula $C_{28}H_{38}O_4N_2$, and F. H. Carr and the present writer[117] have shown that emetine is the mono-methyl ether of cephaeline, and has the formula $C_{29}H_{40}O_4N_2$. In view of the proved relations between the two alkaloids, O. Hesse's[118] new formula $C_{30}H_{40}O_5N_2$, for emetine, may be dismissed. It has now been shown that these alkaloids are derivatives of *iso*-quinoline, and a part of the structure of emetine has been revealed by the isolation from its oxidation products of 6·7-dimethoxy-*iso*-quinoline-1-carboxylic acid,[119]



which, it may be recalled, is also a degradation product of papaverine.

[112] F. Hoffmann-La Roche & Co., Ger. Pat. 289274 (1915), *J.*, 1916, 438.

[113] H. H. Dale, *Brit. Med. Journ.*, Dec. 18, 1915, p. 895; A. Balfour and F. L. Pyman, *Journ. Roy. Army Med. Corps*, Jan., 1916; R. L. Levy and L. G. Rowntree, *Arch. Intern. Med.*, 1916, **17**, 420.

[114] Levy and Rowntree, *loc. cit.*

[115] A. G. DuMez, *Philippine J. Sci.*, 1915, B, **10**, 73.

[116] A. G. DuMez, *loc. cit.*; H. H. Dale, *Lancet*, July 29, 1916, p. 183.

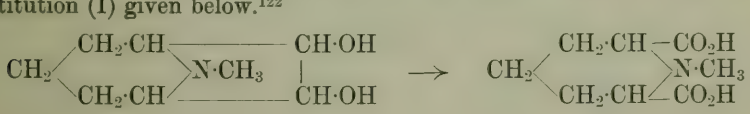
[117] *Chem. Soc. Trans.*, 1914, **105**, 1591; *J.*, 1914, 764.

[118] *Annalen*, 1914, **405**, 1; *J.*, 1914, 610.

[119] Carr and Pyman, *loc. cit.*

Eserine.—F. Straus,[120] in studying the constitution of eserine, has isolated a degradation product of eseroline termed physostigmol, which has the formula $C_{10}H_{11}ON$. Further work on this substance should give important information. M. Polonowski and C. Nitzberg[121] have recorded investigations of eserine in a series of papers. They have effected the partial synthesis of eserine by the action of methyl *iso*-cyanate on eseroline in the presence of a minute quantity of sodium, and have similarly prepared a phenylated homologue of eserine from phenyl *iso*-cyanate and eseroline. They have shown that eserine is accompanied in the Calabar bean by a new alkaloid geneserine, which can be isolated in a yield of up to 0·1 %. Geneserine, $C_{15}H_{21}O_3N_3$, is apparently an oxy-eserine, for it yields eserine on reduction with zinc and acetic acid. Sulphurous acid, however, converts it into a mixture of eserine sulphate and eserine-sulphonic acid.

Hyoscine (*Scopolamine*).—This alkaloid yields on hydrolysis tropic acid and scopoline. Considerable progress has been made in the determination of the constitution of the latter. It has been found that this base combines with hydrogen bromide to yield bromohydroscopoline, $C_8H_{12}NBr(OH)_2$, and the bromine atom in the latter can be replaced by hydrogen by means of reducing agents with the formation of hydroscopoline, $C_8H_{13}N(OH)_2$. The latter yields N methyl-$\alpha\alpha'$-piperidinedicarboxylic acid (II) on oxidation, and thus probably has the constitution (I) given below.[122]



I. II.

Yohimbine.—The identity of the alkaloid yohimbine from yohimboa bark with quebrachine from quebracho-bark was established by Fourneau and Page[123] and confirmed by A. J. Ewins.[124] In spite of these results, however, L. Spiegel, who has studied the chemistry of yohimbine for many years, is not quite satisfied as to the identity of the two alkaloids.[125] Interesting work on the constitution of yohimbine has been carried out by G. Barger and Miss E. Field,[126] who have shown

[120] Annalen, 1913, **401**, 350; 1914, **406**, 332; *J.*, 1914, 40.

[121] *Bull. Soc. Chim.*, 1915, **17**, 235, 244, 290; 1916, **19**, 27, 46; *J.*, 1915, 920, 1070; 1916, 273, 437.

[122] K. Hess and A. Suchier, *Ber.*, 1915, **48**, 2057; *J.*, 1916, 327. E. Schmidt, *Ber.*, 1916, **49**, 164; *J.*, 1916, 379.

[123] *Bull. Sci. Pharmacol.*, 1914, **21**, 7; *J.*, 1914, 373.

[124] *Chem. Soc. Trans.*, 1914, **105**, 2738; *J.*, 1915, 100.

[125] *Ber.*, 1915, **48**, 2084; *J.*, 1916, 327.

[126] *Chem. Soc. Trans.*, 1915, **107**, 1025; *J.*, 1915, 888.

that yohimbine yields a mono- and a di-bromo derivative, and can be converted into yohimbine-sulphonic acid, a sparingly soluble crystalline compound. These facts indicate that the molecule contains a benzene nucleus, and further evidence of the constitution of the alkaloid was afforded by distillation with soda lime, when an ethyl or a dimethyl-indole was obtained, together with a second base, possibly a dimethyl-quinoline.

Glucosides.

The chemistry of the glucosides of *Digitalis purpurea* remains in an unsatisfactory state. It will be remembered that a few years ago F. Kraft[127] described a new physiologically active glucoside, which he isolated from an aqueous extract of the leaves by extraction with chloroform, removal of acidic substances from the chloroformic extract, concentration of this and precipitation by light petroleum. The amorphous product, termed gitalin, was regarded as a pure substance of the formula $C_{28}H_{48}O_{10}$, and was characterized by the formation of a crystalline hydrate with $4H_2O$. Gitalin was said to be very unstable and readily to become dehydrated, yielding anhydrogitalin, $C_{28}H_{46}O_9$. All three substances gave, on hydrolysis with acids, anhydrogitaligenin, $C_{22}H_{34}O_5$, and digitoxose, $C_6H_{12}O_4$. The method of preparation of gitalin does not appear to be likely to furnish a homogeneous product, and it is not surprising that later work has proved this substance to be a mixture. H. Kiliani[128] has shown that it can be separated into at least three distinct fractions—anhydrogitalin, a hydrate, and a residue —which differ in their solubility, physiological action, and hydrolytic products; anhydrogitalin is a constituent and not a degradation product of gitalin, whilst the hydrate is derived from another component of the mixture. L. Rosenthaler's[129] work also confirms the last-mentioned result. Kiliani has shown further that Kraft's anhydrogitalin was probably contaminated by a "genin" obtained by the fission of some glucoside present in gitalin. He has now isolated anhydrogitalin in a pure state, and gives it the formula $C_{33}H_{52}O_{12}$. On hydrolysis it yields Kraft's anhydrogitaligenin, to which the new formula $C_{21}H_{30}O_5$ is attributed, together with digitoxose,[130]

$$C_{33}H_{52}O_{12} + H_2O = C_{21}H_{30}O_5 + 2C_6H_{12}O_4.$$

[127] F. Kraft, *Schweiz. Woch. Chem. Pharm.*, 1911, **49**, 161, 173; *J.*, 1911, 709; Eng. Pat. 28739 (1911), *J.*, 1912, 256; *Arch. Pharm.*, 1912, **250**, 118.

[128] *Arch. Pharm.*, 1914, **252**, 13.

[129] *Schweiz. Apoth. Zeit.*, 1914, **52**, 349; from *Chem.-Zeit.*, 1914, **38**, R. 461.

[130] *Ber.*, 1915, **48**, 334; *J.*, 1915, 680.

The position as regards digitoxin itself is also somewhat obscure, for there are apparently two digitoxins.[131] Both melt at about 240°, when anhydrous, but after crystallization from 85 % alcohol, one form yields a hydrate melting at 145°–150°, whilst the second form remains unchanged. To the first class belong Kiliani's β-digitoxin, Merck's digitoxin of the year 1894–5, and the digitoxins examined by Burmann and Hartung, and to the second Merck's digitoxin of the year 1911–12, and the digitoxin prepared by Kraft. Kiliani[132] has been unable to obtain any explanation of this difference from the firm of E. Merck, who have manufactured digitoxin for many years, but received from them a by-product of the manufacture, which he examined and described. The same author gives an account[133] of a new method of hydrolysis of digitoxin (Merck, 1911–12), whereby digitoxigenin is obtained in a yield of 40·5 %, together with digitoxose. The yield of the sugar could not be determined, as a large amount was unfortunately resinified by treatment with hot dilute (0·5 %) hydrochloric acid. The instability of the sugar in this respect is noteworthy, and explains why Schmiedeberg obtained no sugar by the hydrolysis of digitoxin, and therefore came to the false conclusion that it was not a glucoside. It may be noted that the water-soluble principle of the leaves has recently been prepared in a crystalline state, and is said to be free from digitoxin and saponins.[134]

Some progress has been made in the separation and purification of the glucosides of digitalis seeds based on the fact that some of the constituents of the mixture form crystalline addition products with certain alcohols.[135] *Digitalinum Germanicum* dissolved in dilute alcohol and mixed with amyl alcohol readily yields a crystalline deposit containing the bulk of the digitonin, gitonin, and a new glucoside, which gives on analysis figures agreeing with either of the formulæ $C_{45}H_{72}O_{24}$ or $C_{56}H_{90}O_{30}$. The filtrate from these can be worked up for *Digitalinum verum*, the purification of which has also been described in detail. Previously it had been shown that this glucoside gave on hydrolysis digitaligenin, digitalose, and dextrose, but the latter had not been obtained in crystalline form. Kiliani has now succeeded in effecting its crystallization and thus confirming its identity.[136]

Belonging to the digitalis group of glucosides is the active principle of Canadian hemp, *Apocynum cannabinum*, the nature of which has been

[131] H. Kiliani, *Arch. Pharm.*, 1913, **251**, 580; *J.*, 1914, 216.
[132] *Ber.*, 1915, **48**, 334; *J.*, 1915, 680.
[133] *Arch. Pharm.*, 1913, **251**, 562; *J.*, 1914, 216.
[134] E. Berry, *Pharm. J.*, 1915, **95**, 783; *J.*, 1916, 139.
[135] H. Kiliani, *Ber.*, 1916, **49**, 701; *J.*, 1916, 615.
[136] *Arch. Pharm.*, 1914, **252**, 26; *J.*, 1914, 1071.

made clear by the recent work of A. Windaus and L. Hermanns.[137] They show that this substance, cymarin, has the formula $C_{30}H_{44}O_9$, and yields on hydrolysis with dilute hydrochloric acid cymarigenin, $C_{23}H_{30}O_5$, and a sugar cymarose, $C_7H_{14}O_4$. The latter resembles digitoxose in its reactions, and is probably a methyl-ether of this sugar. Cymarigenin is stated to be identical with the apocynamarin obtained by C. W. Moore[138] from *Apocynum androsaemifolium*; it also proves to be identical with the product of fission of strophanthin-Kombé, strophanthidin, which was previously believed to have the formula $C_{27}H_{38}O_7$.[139] An interesting connection between the three glucosides, digitoxin, cymarin, and strophanthin, is thus established.[140]

$C_{34}H_{54}O_{11} + H_2O$	=	$C_{22}H_{32}O_4$	+	$2C_6H_{12}O_4$
Digitoxin		Digitoxigenin		Digitoxose
$C_{30}H_{44}O_9$	=	$C_{23}H_{30}O_5$	+	$C_7H_{14}O_4$
Cymarin		Cymarigenin (=Strophanthidin)		Cymarose (=Digitoxose-methyl-ether?)
$C_{36}H_{54}O_{15}$	=	$C_{23}H_{30}O_5$	+	$C_{13}H_{24}O_{10}$
Strophanthin-Kombé		Strophanthidin		Strophantibiose-methyl-ether

Attention is drawn to the fact that the above "genins" and also those derived from digitalin and antiarin—other vegetable cardiac poisons—have closely related formulæ, indicating a similarity of their carbon-skeleton.

Chaulmoogra oil and "Gynocardic Acid."

New methods have been described recently for the administration of chaulmoogra oil and its preparations in leprosy, with the object of avoiding the nausea produced when these drugs are given by the mouth. V. Heiser,[141] for instance, gives hypodermic injections of the oil in combination with camphor and resorcin, whilst Sir Leonard Rogers[142] gives sodium gynocardate subcutaneously. Pharmacological experiments have also been carried out with copper gynocardate.[143] Several papers have also been published on the chemical composition of chaulmoogra oil, from which it is clear that there is some confusion in the nomenclature of the acids derived from it. The following notes will show how the confusion has arisen. Chaulmoogra oil is described by

[137] *Ber.*, 1915, **48**, 979; *J.*, 1915, 851.

[138] *Chem. Soc. Trans.*, 1909, **95**, 734.

[139] Compare F. Feist, *Ber.*, 1900, **33**, 2069; *J.*, 1900, 925; D. H. Brauns and O. E. Clossou, *Arch. Pharm.*, 1914, **252**, 294; *J.*, 1915, 680.

[140] A. Windaus and L. Hermanns, *Ber.*, 1915, **48**, 991; *J.*, 1915, 851.

[141] *Lancet*, March 20, 1916, p. 616.

[142] *Ibid.*, Feb. 5, 1916, p. 288.

[143] I. I. Ostromislenskii, *J. Russ. Phys. Chem. Soc.*, 1915, **47**, 335.

the British Pharmacopœia of 1914 as the fatty oil expressed from the seeds of *Taraktogenos Kurzii* (King), and the synonym "gynocardia oil" is applied to the drug. The latter term, which has long been employed, is a misnomer, and owes its origin to the fact that for a long time the seeds from which the oil is expressed were believed to be the product of *Gynocardia odorata* (R. Br.). In 1901, however, E. M. Holmes stated, on the authority of Sir David Prain, Director of the Botanic Survey of India, that the seeds were not derived from *Gynocardia odorata*, but from *Taraktogenos Kurzii*, and subsequently Power and his collaborators[144] showed that the oil expressed from the genuine seeds of *Gynocardia odorata* was entirely different in its characters from chaulmoogra oil. Now, whilst the drug was still regarded as gynocardia oil, Moss,[145] in 1879, separated a fraction of the total fatty acids of the oil, melting at 29·5°, and called it "gynocardic acid." Later, in 1892, Petit[146] published another method for the preparation of "gynocardic acid," this product also melting at 29°. The term "gynocardic acid" has also been applied commercially to the total fatty acids obtained on hydrolysis of chaulmoogra oil. Now that it is generally recognized that chaulmoogra oil is not gynocardia oil, there is a natural tendency to re-name the fatty acids of the oil and their salts chaulmoogric acid and chaulmoograte.[147] This is unfortunate, however, for these names have already been applied to certain pure chemical compounds by Power and Gornall.[148] In the course of a long investigation these authors isolated from the total fatty acids of chaulmoogra oil a new characteristic and well-defined crystalline acid in a pure state. This acid had the composition $C_{18}H_{32}O_2$, melted at 68°, and was termed by the discoverers chaulmoogric acid. I. I. Ostromislenskii and A. M. Bergmann[149] have now rediscovered Power and Gornall's chaulmoogric acid, being apparently unaware of the work of these authors. They isolated the compound from commercial "gynocardic acid," and have called it "pure gynocardic acid." Another instance of the lack of proper appreciation of previous work is presented by the paper of P. C. Chattopadhyay,[150] which deserves notice only from the fact that

[144] Compare especially F. B. Power and F. H. Gornall, *Chem. Soc. Trans.*, 1904, **85**, 838, and F. B. Power and M. Barrowcliff, *ibid.*, 1905, **87**, 896; *J.*, 1904, 669; 1905, 741.

[145] *Yearbk. Pharm.*, 1879, 523.

[146] *J. Pharm. Chim.*, 1892, **26**, 445.

[147] Compare Sir L. Rogers, *loc. cit.*; W. H. Martindale, *Lancet*, April 8, 1916, p. 790; M. A. Rakuzin and G. D. Flier, *J. Russ. Phys. Chem. Soc.*, 1915, **47**, 1848; *J.*, 1916, 366.

[148] *Loc. cit.*

[149] *J. Russ. Phys. Chem. Soc.*, 1915, **48**, 318.

[150] *Amer. J. Pharm.*, 1915, **87**, 473; *J.*, 1915, 1102.

it has called forth a very clear exposition of the distinction between chaulmoogra and gynocardia oils from Power.[151]

The Active Principle of the Pituitary Body.

Reference to the patent literature shows that several attempts have been made to obtain the therapeutically active constituent of the pituitary body in a crystalline form.

The Farbwerke vorm. Meister, Lucius, und Brüning[152] precipitate the active principle with an alkaloid-precipitant such as phosphotungstic acid, remove the precipitant, and convert the product into the sulphate, when it forms pale yellow crystals. H. Fühner[153] throws further light on this product and the *rationale* of its preparation. It appears that the residual liquor after the removal of the phosphotungstic acid precipitate has only a slight activity, and contains a mixture of at least four substances. The crystalline sulphate obtained from the phosphotungstic acid precipitate is stated to be employed in 0·1 % solution under the name "hypophysin." It is not homogeneous, for Fühner has separated it into four fractions, all of which are physiologically active, but vary in the nature of their action and in physical properties. Three of them give Pauly's histidine reaction.

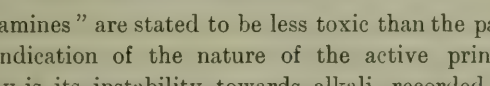
F. Hoffmann-La Roche & Co.[154] obtain a separation of the active principles of pituitary gland in the following manner: The glands are extracted with aqueous sodium carbonate, and the solution is extracted with chloroform. The chloroform extract yields a crystalline hydrochloride which has the pharmacological action on the intestines ascribed to hypophysis extracts, whilst the substances which affect the blood-pressure and uterus are insoluble in chloroform, but can be extracted with alcohol.

In a later patent of the same firm[155] the active principle is separated from inert material by solution of the hydrochloride in absolute alcohol, and precipitated by means of ether when it is obtained crystalline.

So far it has not been possible to isolate substances of undoubted homogeneity and to establish their constitution by analysis. There are, however, some indications of the possible nature of the active principle. Thus, the crystals obtained by Meister, Lucius, und Brüning gave Pauly's histidine reaction, and T. B. Aldrich[156] has also observed that

[151] *Amer. J. Pharm.*, 1915, **87**, 493; *J.*, 1915, 1214.
[152] Ger. Pat. 268841 (1912), *Chem. Soc. Abs.*, 1914, i, 756.
[153] *Deutsch. Med. Wochenschr.*, 1913, **39**, 491.
[154] Ger. Pat. 282002 (1913), *J.*, 1915, 686.
[155] Ger. Pat. 284148 (1913), *Centralbl.*, 1915, i, 1390.
[156] *J. Amer. Chem. Soc.*, 1915, **37**, 203; *J.*, 1915, 12

pituitary preparations obtained from the posterior lobe give this colour-reaction. Moreover, the latter author has observed this colour-reaction with the product which had previously been treated with benzoyl chloride and sodium carbonate, a process which serves to mask phenolic substances, such as tyrosine, and histidine in combination.[157] He concludes that histidine or some similar substance is present, but H. Pauly[158] points out that the diazo-test is not specific for histidine, and only indicates the presence of this substance when other substances capable of coupling with a diazonium salt are known to be absent. The positive reaction of pituitary preparations in the diazo-test gains interest from the fact that in some respects the action of pituitary extract resembles that of β-iminazolylethylamine,[159] which also gives this reaction, and in this connection it may be noted that M. Guggenheim[160] has prepared several "peptamines" or proteinogenous amines from this base and from *p*-hydroxyphenylethylamine. β-Iminazolylethylamine, for instance, combines with chloroacetylchloride in the presence of alkali to give chloroacetyl-β-iminazolylethylamine, which yields with ammonia glycyl-β iminazolylethylamine :—



These "peptamines" are stated to be less toxic than the parent amines.

Another indication of the nature of the active principle of the pituitary body is its instability towards alkali, recorded by Guggenheim.[161] This author suggests that the active principle is an ester-like derivative of an alkanolamine with an acetyl residue, and draws attention to certain chemical and pharmacological resemblances between it and acetylcholine. The latter substance has recently been studied by H. H. Dale[162] and A. J. Ewins,[163] who isolated it from ergot. A number of physiologically active esters and ethers of choline have also been described.[164]

Essential Oils.

During the period under review a number of useful and informative articles have appeared on the above subject. The special numbers of

[157] Compare K. Inouye, *Zeit. physiol. Chem.*, 1912, **83**, 79.

[158] *Zeit. physiol. Chem.*, 1915, **94**, 426; *J.*, 1915, 1225.

[159] H. Fühner, *Münch. Med. Wochenschr.*, 1912, **59**, 852.

[160] *Biochem. Zeitschr.*, 1913, **51**, 369; F. Hoffmann-La Roche & Co., Ger. Pat. 281912 (1913), *J.*, 1915, 735.

[161] *Biochem. Zeitschr.*, 1914, 65, 189.

[162] *J. Physiol.*, 1914, **48**, iii (*Proc.*).

[163] *Biochem. J.*, 1914, **8**, 44; *J.*, 1914, 664.

[164] A. J. Ewins, *Biochem. J.*, 1914, **8**, 366; *J.*, 1914, 1027.

the *Perfumery and Essential Oil Record* for 1915 and 1916 contain a treatise on the chemistry, analysis, and technology of essential oils with notes on other natural perfumery products,[165] and a dictionary of essential oils with bibliographic references containing an index to common names.[166] Monographs on a large number of individual essential oils have also appeared in the same journal.

The effect of the war on the prices of essential oils has been recorded in a list showing the prices from month to month.[167] The employment of essential oils in war is exemplified by their use as antiseptics in the treatment of wounds[168] and as parasiticides.[169] An interesting general article on their employment in medicine has appeared,[170] besides special articles on the use of eucalyptus oil in spotted fever[171] and scarlet fever,[172] and on the use of oil of chenopodium in hookworm disease.[173] The manufacture of synthetic perfumes is discussed by J. Dupont,[174] and the synthetic productions of artificial musk[175] and of vanillin[176] have also been described. It may be noted that English manufactures of the following were displayed at the meeting of the London Section of this Society on March 1, 1915:—cineol, menthol, oenanthic ether, thymol, vanillin, terpene hydrate, and terpineol.[177]

Amongst the subjects to which much attention has recently been paid are the manufacture and sources of thymol, and the determination of cineol in eucalyptus oil.

Thymol.—This important derivative of many essential oils was manufactured chiefly in Germany before the war from the essential oil of ajowan seeds obtained from India, and consequently after the outbreak of war the price of this substance rose considerably. Much useful information has since been published not only on the manufacture of thymol from ajowan seeds,[178] but also on other essential oils which contain this substance in quantity. Different species of *Origanum* contain either thymol or carvacrol, or both; thus Cyprus origanum oil (from *O. majoranoides*) contains 78 to 84 % of carvacrol, whilst the oil of *O. hirtum* contains 66 to 67 % of thymol but no carvacrol.[179] Attention has also been drawn to other sources of thymol, such as oil of thyme and

[165] J. C. Umney and C. T. Bennett, *Perf. and Essent. Oil Rec.*, 1915, **6**, 142; *J.* 1915, 740.

[166] *Ibid.*, 1916, **7**, 152.

[167] *Ibid.*, 1914, **5**, 429.

[168] W. H. Martindale, *ibid.*, 1914, **5**, 58.

[169] *Ibid.*, 1916, **7**, 4.

[170] *Ibid.*, 1916, **7**, 8.

[171] *Ibid.*, 1915, **6**, 305.

[172] *Ibid.*, 1916, **7**, 3.

[173] *Ibid.*, 1915, **6**, 104, 125.

[174] *Ibid.*, 1915, **6**, 283, 307.

[175] *Ibid.*, 1916, **7**, 133.

[176] *Ibid.*, 1916, **7**, 248.

[177] *Ibid.*, 1915, **6**, 77; *J.*, 1915, 258.

[178] *Ibid.*, 1915, **6**, 255.

[179] E. M. Holmes and J. C. Umney, *ibid.*, 1913, **4**, 7, 41, 69; *J.*, 1913, 378.

American horsemint (*Monarda punctata*).[180] It is satisfactory to note that thymol is now being made from ajowan seeds both in this country[181] and in India,[182] whilst the seed has been introduced into the West Indies for the purpose of cultivation.[183]

Cineol in eucalyptus oil.—The resorcinol method for the determination of cineol in eucalyptus oil, previously condemned as unreliable by J. C. Umney, has now been criticized both by H. G. A. Harding,[184] and by J. L. Turner and R. C. Holmes.[185] The latter authors find that the crystalline addition product of cineol and arsenic acid is sufficiently stable to permit of its being handled in the air, and they propose a method of analysis of eucalyptus oils based on this finding. It is, however, by no means established that cineol is, in a therapeutic sense, the active principle of eucalyptus oil.[186]

[180] J. C. Umney, *ibid.*, 1914, **5**, 372; *J.*, 1914, 1073; *Bull. Imp. Inst.*, 1914, **12**, 599; *J.*, 1915, 301.

[181] *Pharm. J.*, 1915, **96**, 311.

[182] *Perf. and Essent. Oil Rec.*, 1916, **7**, 125; *J.*, 1916, 652.

[183] *Ibid.*, 1916, **7**, 266.

[184] *Analyst*, 1914, **39**, 475; *J.*, 1914, 1171.

[185] *Pharm. J.*, 1915, **94**, 60; *J.*, 1915, 150.

[186] J. C. Umney, *Perf. and Essent. Oil Rec.*, 1915, **6**, 20; *Chemist and Druggist of Australasia*, from *Perf. and Essent. Oil Rec.*, 1915, **6**, 206.

PHOTOGRAPHIC MATERIALS AND PROCESSES.

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There is not very much to report in the way of definite progress in the photographic industry since the beginning of 1915. The only European countries in which the industry is carried on to any considerable extent are either directly engaged in the present war—Great Britain, France, Belgium, and Germany—or very closely associated with these commercially, and the attention of manufacturers in these countries has been directed more to meeting new conditions, both as to labour and as to supplies of raw material, than to the introduction of new processes. America also has been affected by the war, though naturally to a less extent. There is, of course, continued improvement being effected in details—questions of gradation, freedom from mechanical defects, keeping quality, and general economy—but almost all emulsion making is carried on by secret processes, and considerable alterations and improvements, even to the extent of the introduction of quite new processes, can be made without there being anything tangible to report.

In European countries generally there has been a very appreciable decrease of production due to the war, though less than was at first feared. There do not appear, however, to be any statistics available to show either that decrease or the general and steady increase which was evidenced before the war. The increased trade in X-ray plates has to a small extent balanced the loss, and it is probable that some of the increase will remain after the war, as the value of X-ray examinations has become much more commonly known, and X-ray apparatus has been installed in many hospitals which were previously without it. Export trade has undergone some rearrangement, as Germany's share of this has been almost entirely cut off. America is absorbing part of this as her production has increased, so that she now not only supplies practically all her own requirements, but is also competing with European countries, especially in Japan, China, and South America.

Raw Material.

Of the chief chemicals used in photographic manufactures, bromides have been most affected by the war. The supply of bromine was practically limited to Germany and the United States, and the almost complete cessation of German exports, except such as may have got through Switzerland, has caused the price of bromides to rise from 2*s*. to as high as 25*s*. per lb., though it seems to have settled down now to a fairly steady price of about 5*s*. per lb. Gelatine has been gradually increasing in price since the war broke out and is now about double its pre-war price. There was a considerable quantity of German gelatine in use, and the British, Swiss, and French gelatines have not quite the same qualities. The production of British emulsion gelatine has been very much increased, and considering especially the difficulties which the makers have experienced owing to the shortage of first-class raw materials, there is every reason to expect that a good deal of this increase will be permanent. American factories are supplying American requirements, but very little seems to have been exported to England. It would appear to be a very specialized manufacture, as a considerable quantity of gelatine has been offered for photographic use which could find only a very limited application. In this connection the process patented by the Gesellschaft für Elektro-Osmose[1] in Frankfort is worth mention. An electric current is passed between indifferent diaphragms in the gelatine solution, so that mineral impurities are separated and albumins are afterwards easily filtered off.

The price of glass, which was already rising before the outbreak of war, has risen further by 70 to 100 per cent., the complete withdrawal of Belgian supplies being partly responsible.

The supply of photographic raw paper has been much reduced. The French mills have kept in work, though with a smaller output, and they have been able to do very little baryta coating. A certain increase in British output has resulted, both of paper and of baryta coating, but there has been a distinct shortage. The price has advanced considerably in line with that of other papers, of which, of course, large quantities are used for packing purposes.

Roth[2] has patented a process in which fatty soaps and other substances giving insoluble silver salts are mixed with the size used in making photographic paper, so as to improve the keeping quality by preventing the passage of soluble silver salts into the paper.

Other more or less important chemicals have been variously affected

[1] Eng. Pats. 21448 and 21484, 1914, *J*., 1915, 971 and 1072.
[2] Ger. Pat. 285562, 1912, *J*., 1915, 1168.

in price or supply, and some have been entirely cut off: there has been, for instance, in Germany a shortage of silver nitrate and of citric acid. Potassium ferricyanide, the basis of the blue print process, has risen considerably in price, and the American Department of Agriculture[3] has worked out a new and cheaper method for producing it by the reaction between the ferrocyanide and chlorine, purification from the chloride also produced being unnecessary.

The chief sensitizing dyes used in the production of panchromatic plates were entirely produced by Meister, Lucius, und Brüning, of Hoechst, and the supply both here and in America has been nearly exhausted. The possibility of replacing them with British-made dyes has been considered, and it appears certain that this will shortly be achieved.

The effect of this general increase in cost of raw materials, combined with increased working and labour costs, has been a general advance in prices of almost all plates and papers of from 50 to 80 per cent.

Negative Processes.

Apart from the general improvements already mentioned there is little to report in the way of new productions. Messrs. Ilford Limited and Paget have each introduced a new plate for quick process work, characterized by very rapid development, fixation, etc. This is apparently obtained by having a thin coating of an emulsion of hard gradation and great density, and with a minimum of gelatine.

The increased production of X-ray plates has not been marked by serious improvement in quality, although there is a larger number of firms producing good plates. There is some demand for a much faster plate, as short exposures are at present obtained, either by the aid of an intensifying screen, which, though reducing the exposure by about 90 per cent., is not entirely satisfactory, or by the use of specially powerful and expensive apparatus necessitating considerable expense in renewals. E. C. Saleil[4] has patented the use of a double film, with or without a support, one part being a celluloid film containing calcium tungstate and the other the sensitive film; this is of course the combination of an intensifying screen with the sensitive film, and is hardly likely to be commercially practicable unless fluorescent calcium tungstate can be produced by a much cheaper method than at present. Arnold and Levy-Dorn[5] have taken out a

[3] *B.J.*, 1916, 281; *J.*, 1916, 944.

[4] Fr. Pat. 468806, 1913, and addition, *J.*, 1914, 986; 1915, 50.

[5] Eng. Pat. 2243, 1915, *J.*, 1916, 386.

patent for the incorporation of thorium hydroxide, tungstic acid, and other heavy bodies with a great opacity for X-rays in emulsions for radiographic use. There are already two X-ray plates on the market in which these ideas have been utilized, one of them containing a fluorescent salicylate, and the other an opaque bismuth salt, but for various reasons they have not succeeded in establishing a general superiority over the other makes of plate.

Lehmann and Knocke[6] have patented a process for ripening albumin emulsions by heat, excess nitrates being first removed by dialysis and other salts then added.

S. Cocanari[7] has patented a peculiar process in which a deep blue or deep violet film is used as an antihalation backing. Sosna and Biedebach[8] add a blue or violet dye to the film so as to reduce the sensitiveness to dark-room light without reducing daylight-sensitiveness.

Hommel,[9] in Germany, and Cossitt and Castor,[10] for the Ansco Company in America, have taken out patents for vacuum drying, the former for plates, the latter for paper or film, with arrangements for recovering the solvents from collodion emulsions. The former is not a new idea in this country, as vacuum drying plants have been made for some time which could be adapted to the drying of plates with very little difficulty.

Paris and Picard[11] have protected the use of phosphorescent substances, such as zinc sulphide, either in the emulsion or as a separate film, for the purpose of increasing the speed as in the use of calcium tungstate for radiographic plates.

Lüppo-Cramer[12] finds that collodion emulsions suitable for making wet plates, can be made suitable for dry plates by the addition of resinous substances, especially Canada balsam; the plates do not keep well.

Positive Processes.

There is a considerable amount of fashion in the selection of papers for photographs, and new grades of paper, with variations in surface, etc., are being constantly introduced to meet a prevailing fashion, or as

[6] Ger. Pat. 288076, 1914, *J.*, 1916, 386.
[7] Fr. Pat. 469218, 1914, *J.*, 1915, 50.
[8] Ger. Pat. 288328, *J.*, 1916, 386.
[9] Ger. Pat. 286933, 1914, *J.*, 1916, 199.
[10] U.S. Pats. 1171321, Feb. 8, 1916, and 1180255, Apr. 18, 1916, *J.*, 1916, 386 and 655.
[11] Fr. Pat. 477173, 1914, *J.*, 1916, 617.
[12] *Koll. Zeits.*, 1915, 105; *J.*, 1916, 708.

novelties. There is a considerable amount of work being done in toned bromide and gaslight prints, and the preference for a paper may be because of the ease of toning it by a special method. Schering[13] has patented tellurium toning baths. Sulzberger[14] has taken out a patent in Germany for the use of ferrocyanide as a desensitizer for silver chloride papers; in the case of gaslight papers, subsequent development is not interfered with; with P.O.P., after desensitizing, the image may be bleached with ammonium ferrocyanide and then developed to a black image.

Balconi[15] has brought out a process for quick production of a print in which he uses a double film consisting of a slow and a fast emulsion; exposure for the positive is made after development of the negative, which is then stripped off and the development of the positive carried on.

J. Bekh[16] has examined silver azide and protected its use for the production of print-out emulsions.

The increasing price of platinum, even before the war, had seriously interfered with the production of platinum papers, but the Platinotype Company have met the difficulty by the introduction of Satista paper.[17] This is a combined ferric oxalate-silver paper containing a small quantity of a platinum salt, and is handled in very much the same way as a platinum paper. The platinum salt considerably increases the density of the image and also takes part in its formation, the lighter tones being almost entirely platinum. In general effect and permanence the image is very similar to a platinum print.

A somewhat similar process has been patented in America by Rubricius,[18] who uses a sensitizing solution containing ferric ammonium citrate, silver nitrate, and uranyl nitrate.

Valenta[19] has examined the effect of various additions to the usual blue print sensitizer—green ferric ammonium citrate with potassium ferricyanide. Lüppo-Cramer[20] has made experiments on the continuating action of yellow light, and indicates how this can be carried out; he suggests, as an explanation, the formation of traces of colloidal silver

[13] Ger. Pat. 271041, 1912, *J.*, 1914, 503; and Ger. Pat. 290270, 1915, *J.*, 1916, 617.

[14] *Phot. J. Amer.*, 1915, 405; *Atel. de Phot.*, 1915, 47.

[15] Fr. Pat. 466996, 1914, *J.*, 1914, 845.

[16] *Z. wiss. Phot.*, 1914, **14**, 105; *Z. angew. Chem.*, 1915, **28**, Ref. 93, *J.*, 1915, 637.

[17] W. Willis, Eng. Pat. 20022, 1913, *J.*, 1914, 986; also *Phot. J.*, 1915, 282–285.

[18] U.S. Pat. 1126872, Feb. 2, 1915, *J.*, 1915, 303.

[19] *Phot. Korr.*, 1915, 217; *Phot. J. Amer.*, 1915, 545.

[20] *Phot. Ind.*, 1915, Heft 16; *Z. angew. Chem.*, 1915, **28**, Ref. 533; *J.*, 1915, 199.

in the first exposure, which act as sensitizer for the further exposure to yellow light.

J. J. Robinson[21] has patented the use of bichromated fish glue on mica for the production of lantern slides, and Travers[22] has adopted a similar idea for lantern slides, and for intaglio or relief printing plates, except that he obtains them by printing in a coloured ink composed of a gum dissolved in petroleum or naphtha with a dye ground in; in both cases the slides or plates are dried off and hardened by heat.

Sury[23] has taken out patents for a carbon process, using powdered glass for producing a rough surface.

Brixey[24] has adapted the multi-colour starch grain screen idea to the formation of a translucent projection screen, the lantern being on the side of the screen away from the spectators.

Rosenberg,[25] in order to keep a hardened gelatine relief printing plate in a proper degree of dampness, uses a porous support of fireclay, or similar material, containing glycerin.

Knudsen[26] has two patents for a photo-mechanical screen, consisting of hemispherical globules, preferably coloured, of a substance such as asphalt on a transparent support.

Colour Processes and Cinematography.

By far the greatest part of the activity of photographic inventors is directed to the solution of the problem of photography in colours, and especially with its extension to cinematography. There have been, of course, for some time, several methods in use for the production of colour photographs, both multi-colour screen methods and multiple film methods, but none of these can be regarded as entirely satisfactory, and the adaptation of any method to cinematograph films is attended with very considerable mechanical difficulties. The multi-colour screen method is inevitably accompanied by the serious drawback of lack of transparency, as even the whites transmit not more than one-third of the incident light, while the production of the screens themselves, in the form of cinema films, is very difficult. On the other hand, the use of a multiple film, or of a single film with alternating sets of pictures, involves either special projection apparatus or considerable difficulty in

[21] Eng. Pat. 24103, 1913, *B.J.*, 1915, 58.
[22] Eng. Pat. 5363, 1915, *B.J.*, 1916, 284.
[23] Eng. Pat. 21958, 1913, *J.*, 1914, 43, 44.
[24] Eng. Pat. 8805, 1913, *B.J.*, 1915, 26.
[25] Eng. Pat. 26140, 1913, *J.*, 1915, 889.
[26] Eng. Pats. 2817 and 2818, 1914, *J.*, 1915, 890 and 924.

registration. The Kinemacolor process has met with some success commercially, but it is only a two-colour process and requires a special lantern. The efforts of inventors seem to be chiefly directed to surmounting the difficulties of registration in the making of a three-colour positive film which can be used in an ordinary projection lantern.

Of the new processes which have lately been introduced, only one is adapted to cinema work. This one, Kodachrome,[27] based on Capstaff's patents,[28] and brought out by the Kodak Company, is a two-colour process, and for this reason restricted in its application, as only a limited range of colours is reproducible by a two-colour process, the actual range being dependent upon the complementary colours chosen. Jones[29] has an interesting paper on this subject, in which he analyses the full range of tones which can be obtained by the mixing of two complementary colours; the problem is, of course, twofold, according to whether the process is additive as in Kinemacolor, or subtractive as in Kodachrome; but the limits are quite definite in each case. The complementary colours of the Kodachrome process have been specially selected for adaptation to portrait work, and very good flesh tints are possible. Two negatives are taken through colour screens, bleached in an acid solution of ferricyanide, bromide, bichromate, and alum, which hardens the gelatine according to the depth of the silver image, and then stained up with a dye complementary in each case to the taking screen, the dye entering the gelatine in inverse proportion to the amount of silver image in the negative.

The Hicro[30] process, based on H. E. Ives' patents and brought out by the Hess-Ives Corporation, and the Polychromide process of Hamburger,[31] are both three-colour processes in which three plates are simultaneously exposed in a specially adapted camera. In the Polychromide process a platinized reflecting filter is used, passing red and reflecting blue and green; the blue-sensitive and green-sensitive films are face to face, the one acting as filter for the other. The three positives are all obtained from silver prints on a special bromide paper, the yellow by bleaching in a bath which leaves, after washing, an image of silver and mercury iodides, the blue by conversion into Prussian blue, and the red by treatment with alizarin, which forms a lake with the silver image. They are superposed in register on glass and transferred to paper.

[27] *Phot. J.*, 1915, 140–142.
[28] Eng. Pats. 13429, 13430, 1915, *J.*, 868 and 907.
[29] *B.J. Colour Supplement*, 1915, Feb., Mar., and Apr., pp. 6–8, 11, 13–14.
[30] *Ibid.*, 1915, 34–36.
[31] *Phot. J.*, 1914, 288–293.

In the Hicro process the red and green sensitive plates are behind the reflector, and the blue at right angles; the green sensitive plate acts as filter, or carries a filter, for the red-sensitive. In making transparencies, special films are used which are exposed through the celluloid, developed in hot water, fixed in hypo, followed by ferricyanide to remove the silver salts, and then stained up with special dyes. For prints on paper the blue print is made on a ferroprussiate paper. The three prints are superposed in register.

A number of patents have been published, both for multicolour screens and for various details in the production of positives. In the latter, apart from the mechanical difficulties of registration, the chief problem appears to be to get a method of colouring which will give a uniform tone throughout the length of a film: methods in which the amount of colour is dependent on the strength of the image rather than on the gelatine of the film appear to be generally preferred. There seems to be a certain amount of overlapping, practically the same ideas occurring in different patents.

In processes for multicoloured films, Dufay[32] has added to his original patent a method in which he starts with a colourless transparent film in relief, fills up the hollows with one colour, stains the remaining surface to another colour, prints in a greasy ink, and then stains for the last colour. Rheinberg[33] uses a method in which he takes advantage of the change of permeability of a film to solvents due to light action, the colour being thus abstracted from parts of an underlying coloured film after exposure through a screen. (See also Christensen.[52]) Thornton[34] produces screens by successive printings with intaglio engraved rollers or plates with various devices to ensure uniformity and correct registration, and arranging in the case of continuous films for a stagger of the design from one picture to the next so that the pattern shall not be visible on the screen. Petzold[35] makes two successive printings on bichromate sensitized gelatine films, staining with a red and a green acid or azo dye which is fixed by the reduced chromate; the remaining spaces are stained with a blue rosaniline dye. Brasseur[36] produces screens very similar to the Krayn screen, starting with strings of transparent coloured colloid (*e.g.*, celluloid), which are cemented into blocks and sections cut off; by a suitable arrangement of the blocks round a core, continuous films can be obtained in a

[32] Fr. Pat. 442881, 1911, second addition, Mar. 20, 1914, *J.*, 1916, 73.
[33] Eng. Pat. 9929, *J.*, 1915, 637.
[34] Eng. Pat. 14145, 1914, *J.*, 1915, 852.
[35] Ger. Pat. 279932, 1913, *J.*, 1915, 453.
[36] Eng. Pat. 28631, 1913, *J.*, 1915, 303.

similar manner to cutting veneers. Wieland and Mohr[37] in Germany and Bleecker[38] in America have patented the process of obtaining multicoloured screens of glass by blowing finely powdered coloured glass on to a glass sheet with air just hot enough to soften the particles without making them coalesce, and taking precautions to ensure obtaining a single layer of particles.

Capstaff's patents[28] include an arrangement for two-colour printing on either side of a cinematograph film coated on both sides, a method very similar to that of Brewster,[39] who also uses double-coated film. Caille[40] takes a three-colour screen negative, and prints from it through light filters, a process also used by Ungerer.[41] After the first printing and staining he resensitizes, prints and stains again, and then re-coats with sensitive emulsion for his last colour. Cox[42] uses a very similar method, but takes three separate negatives through colour screens. Caille also uses for his yellow image a mixed mercury-silver iodide, which appears to be the same compound as used in the Polychromide process. Buchanan Taylor and others[43] also use a similar method to Caille's, but vary the order of printing, the yellow print being the last one, and this they may obtain as a separate print, and then transfer by imbibition to the film holding the two other images; or they get a silver image first, then sensitize twice for two of the colours, and finally tone the first image. Lewisohn[44] also has three printings on one base, but each print is first made in ferroprussiate, then the colour is applied, and the ferroprussiate image removed by silver nitrate. Kinemacolor, Limited, with Fox and Hickey,[45] have a two-colour process in which a print from a composite negative, made with a negative from one colour and a positive from the other colour, is toned green by vanadium and a dye and stained red, a method very similar to the one previously adopted by Donisthorpe.[46] Donisthorpe also makes use of a "key" print in black and white combined with the colour print, apparently to increase the brilliance and to give a slight colour correction. The same idea has been adopted by Zoechrome, Limited, a

[37] Ger. Pat. 283551, 1913, *J.*, 1915, 1168.

[38] U.S. Pat. 1175224, Mar. 14, 1916, *J.*, 1916, 490.

[39] Eng. Pat. 2465, 1913; Fr. Pat. 468297, 1914, *J.*, 1914, 986 also Eng. Pat. 1073, 1915, *J.*, 1916, 329.

[40] Fr. Pat. 463062, 1912, and additions Dec. 9, 1912, and Dec. 6, 1913, *J.*, 1914, 440, and 1915, 1118.

[41] Eng. Pat. 17979, 1913, *J.*, 1914, 222.

[42] Eng. Pat. 15648, 1914, *B.J.*, 1915, 673–4.

[43] Eng. Pats. 21778, 1913, *J.*, 1915, 199, and 20433, 1914, *J.*, 1916, 276.

[44] Eng. Pat. 2474, 1915, *J.*, 1916, 754.

[45] Eng. Pats. 552 and 8728, 1914, *J.*, 1914, 1227.

[46] Eng. Pat. 7368, 1913, *J.*, 1914, 503.

company formed to work up T. A. Mills' patent,[47] a three-colour single-film process, the negative being a single film taken through alternating filters. Kinemacolor have another two-colour patent with C. K. Mills,[48] using the vanadium toning and dye method for the green print, superposed on a Prussian-blue print. An alteration in the absorptive power of gelatine for dyes is used in the Rotophot Company's process,[49] where the hardening is that produced by exposure of a bichromated film, and in Thornton's[50] and Capstaff's[28] processes, where bleaching of the silver image and hardening are carried out together, while in another of Thornton's patents[51] the dye (of the Chromotrope or Erio group) is mordanted by the reduced chromium salt (see also Petzold[35]). Christensen[52] makes use, for transfer of colour, of the variation, according to the amount of image, in the permeability of developed celluloid film, the emulsion for which has been made with a solvent such as mixed amyl acetate and methyl alcohol, giving a film with uniformly distributed silver salt. Ives[53] transfers colour from one film to another by pressing together with merely a thin film of solvent between. Ives[54] has also a two-colour process in which the red image is superposed on the insoluble blue-green image, and also patents[55] the process of exposure of two or three sensitive films through one or two of them, with addition of suitable colour filters or arranging for the upper films to act as filters for the lower ones. Schweitzer's process[56] depends on the use of oxidizable dyes and oxidizing agents, the latter being affected either by direct light action (*e.g.*, manganese lactate or oxalate) or by a silver image (chromate and permanganate).

The problem of finding a satisfactory non-inflammable substitute for celluloid does not appear to have been finally solved as yet, for although various preparations of cellulose, such as the acetate (Cellit[57]) and viscose, are on the market, and much used for other purposes, the greater part of cinematograph film is still made of celluloid. Viscose film is much too water-absorbent. Balland and Company[58] render it

[47] Eng. Pat. 28081, 1912.
[48] Eng. Pat. 3666, 1915, *J.*, 1916, 73.
[49] *Phot. Rund.*, 1915, 214; *Phot. J. Amer.*, 1916, 35.
[50] Eng. Pat. 13711, 1914, *J.*, 1915, 818.
[51] Eng. Pat. 29113, 1912, *J.*, 1914, 278.
[52] Eng. Pats. 25419, 1913, and 13260, 1914, *J.*, 1914, 1226, and 1915, 199.
[53] Fr. Pat. 463737, 1913; Eng. Pat. 15823, 1913, *J.*, 1914, 441.
[54] U.S. Pat. 1170540, Feb. 8, 1916, *J.*, 1916, 386.
[55] U.S. Pat. 1173429, Feb. 29, 1916, *J.*, 1916, 490.
[56] Fr. Pat. 476213, 1915, *J.*, 1916, 73–74.
[57] *Phot. J.*, 1913, 10–12.
[58] Fr. Pat. 473189, 1913, *J.*, 1915, 513.

impervious to water by a coating of celluloid varnish, which is followed by a coating of glue or gelatine containing also a resin soluble in celluloid solvents in order to cause adherence of the sensitive film. Pathé Frères[59] add polymers of isoprene or similar substances in acetone or methyl acetate solution to the cellulose acetate solution in order to cause impermeability. On the other hand, the Société Anonyme la Collophane[60] utilize the permeability of a viscose film for the protection of the gelatine film from abrasion in the lantern; a composite film of celluloid, sensitive film, and viscose is used, the development, fixation, etc., taking place through the viscose. Several patents for treatment of scratched and abraded cinema films with various oils and fats have been taken out by Hochstetter and Pierson.[61]

Developers, etc.

The effect of the war on developing reagents has been very marked. A considerable supply of all developers came from Germany, especially metol, amidol, and *p*-aminophenol. Pyrogallic acid has risen appreciably in price, while the prices of hydroquinone, metol, amidol, etc., have increased by anything from 200 per cent. to 400 per cent. In 1914 the *Chemist and Druggist*[62] published a list of all the commonest developers, with formulæ and general methods of manufacture. British manufactures have been considerably stimulated in pyro, amidol, and quinol, and several metol substitutes have been introduced; the prices have been maintained, however, at a high level. The shortage has also been felt in Germany and in America, where several factories have started making developers, while amidol and quinol are also being made in Australia. *p*-Aminophenol is at present almost unobtainable in this country, except in so far as it is used for the production of concentrated single-solution developers. Numerous formulæ have been suggested in the photographic papers for developers using pyro where amidol or metol-quinol is ordinarily preferred. J. L. Lizius[63] recommends the recovery of quinol from used developers by a reduction and distillation process, but it is hardly likely that the method will be economically applicable, except, perhaps, for large users, such as process workers. Namias[64] recommends the continued use of

[59] Fr. Pat. 475351, 1914, *J.*, 1916, 73.

[60] Eng. Pat. 2411, 1915, *J.*, 1915, 983.

[61] U.S. Pats. 1139679-1139683, May 18, 1915, *J.*, 1915, 688; Eng. Pat. 9969, 1914.

[62] *Chem. and Drug.*, 1914, **85**, 413–414; *J.*, 1914, 985–6.

[63] *Phot. J.*, 1916, 110–114; *J.*, 1916, 490.

[64] *L'Ind. Chim. Min. e Met.*, 1915, **2**, 462–464; *J.*, 1916, 143.

developers of the metol-quinol type, adding from time to time a little fresh developer, without bromide, and a little sulphite. The writer has found a similar method to answer very well in X-ray work.

Several new developers have been patented, though so far they do not appear to have secured a wide application. Lumière and Jougla[65] have patented chloroquinol-metol, while Seyewetz and Paris[66] have examined bromine derivatives of quinol, and find that, although monobromoquinol is not a developer, its mono-sulphonic acid is. Meister, Lucius, und Brüning[67] have patented the use of oxy-*iso*-carbostyryl for the production of sepia tones, changing to red on removal of the silver image, and also the mono-alkyl ethers of 1.4-dihydroxynaphthalene,[68] which give blue tones in a similar manner. Vidal[69] has patented the use as developers of a number of amino compounds first described in 1908, the Berlin Aniline Works methyl-glycin,[70] a developer easier to use than glycin and about half-way between it and metol in developing qualities, Pellizarri,[71] the aldehyde-bisulphite and acetone-bisulphite compounds of developers such as metol and *p*-aminophenol, which are ready for use on dissolving in alkaline carbonate solutions, and the Elektrochemische Werke,[72] a developer, solid or liquid, in which ferrous oxalate is used in conjunction with a hydroxycarboxylic acid. Thatcher[73] has taken out a patent for the use of *p*-aminophenol sulphate with alkali sulphite, carbonate, and hydrate, but its value would seem very doubtful in view of the already published formulæ for *p*-aminophenol developers.

J. Maldiney[74] describes the effect of sugar as a restrainer in development, which he found to be due to the increased viscosity of the solution lowering its rate of permeation into the gelatine film. Lüppo-Cramer[75] has a series of papers dealing with the action of various salts on developers, and the action of bichromate[76] before development,

[65] Fr. Pat. 468338, 1913; Eng. Pat. 1795, 1914, *J.*, 1914, 986.

[66] *Bull. Soc. Chim.*, 1914, **15**, 121–125; *J.*, 1914, 1226.

[67] *Phot. J. Amer.*, 1915, 406.

[68] Ger. Pat. 284423, 1914, *J.*, 1915, 1168; *Phot. Korr.*, 1914, 471; *Phot. J. Amer.*, 1915, 157.

[69] Fr. Pat. 468537, 1913, *J.*, 1914, 986.

[70] *Phot. Korr.*, 1915, 90; *Phot. J. Amer.*, 1915, 306.

[71] *Annali Chim. Appl.*, 1914, 129–132; *J.*, 1914, 1075.

[72] Ger. Pats. 286727 and 286775, 1914; *J.*, 1916, 199.

[73] U.S. Pat. 1158011, Oct. 26, 1915, *J.* 1915, 1226.

[74] *Compt. Rend.*, 1915, 73–76; *J.*, 1915, 889.

[75] *Phot. Korr.*, 1915, **35**; *Z. angew. Chem.*, 1915, **28**, Ref. 533; *J.*, 1916, 198–199; *Koll. Zeits.*, 1914, 164–166; *Z. angew. Chem.*, 1915, Ref. 190; *J.*, 1915, 687; *Koll. Zeits.*, 1915, 135; *J.*, 1916, 708.

[76] *Phot. Ind.*, 1915, **29**; *Z. angew. Chem.*, 1916, Ref. 41; *J.* 1916, 439.

which is similar to persulphate reduction. Frary and Nietz[77] gave an interesting set of papers describing the results of examination of developers with respect to their single potentials. These are dependent upon the alkalinity of the solution and upon the partial hydrogen pressure which can be calculated, and is taken as a measure of the reducing power.

Theoretical and Experimental.

The problem of the nature of the latent image is still being debated. The electronic theory as explained by Allen[78] and Mees[79] assumes the action of light in a normal exposure to produce only a physical or electrical change in the silver halide, there being no chemical separation of halogen. The separation of one or more electrons from a grain of halide leaves it in unstable equilibrium and easily attacked by developers. The very small amount of energy received in normal exposures is stated as being sufficient to account for the separation of electrons, but not for a chemical separation. The phenomena of reversal and second negative are explained by Allen as being due to a return of the electrons to the parent atom. As more and more electrons are separated from a grain with increasing exposure the positive charge on the grain and the surrounding negative charge grow larger until spontaneous neutralization occurs and the grain reverts to its original condition. Crowther[80] takes a different view. While agreeing that the initial effect of light action is probably electronic, he suggests that this induces chemical separation of the halogen, which either remains as such or is absorbed by some other constituent of the film—the gelatine where this is the medium, or the specially added *p*-phenylenediamine or hydrazine in the case of non-reversal plates. The effect of exposure is quite continuous and not oscillating, as in Allen's view, up to the formation of a print-out image and the evolution of halogen from the film. Reversal and second negative are phenomena, partly of development, due to the gelatine halogen complex and to the print-out image. He supports his theory by the action of developers of the thio-indoxyl type, which give a double image consisting of silver and the oxidized developer. There is reversal of the coloured image along with the silver image, but there is no evidence of the formation of a second coloured negative. He draws attention to the differences between collodion films, where the

[77] *J. Amer. Chem. Soc.*, 1915, **37**, 2246–2279; *J.*, 1915, 1117.
[78] *Phot. J.*, 1914, 175–184.
[79] *J. Frank. Inst.*, 1915, 141–160; *Sci. Abs.*, 1915, 346.
[80] *Phot. J.*, 1914, 249–260, and 1915, 186–199.

medium is not a bromine absorber, and gelatine films, where the medium is a bromine absorber. In this connection it is worth while to mention an experiment by Lüppo-Cramer[81] showing that while, generally speaking, in the case of gelatine emulsions, an increase in size of the halide grain is accompanied by an increase of speed, in the case of collodion emulsions the reverse is the case, an increase in size of grain being accompanied by a reduction in speed. Professor Wood's statement as to the effect of superposing various stimuli on photographic plates, reversal being obtained in some cases, is explained by the electronic theory and used in support of it. Without knowing the exact conditions of Wood's experiments, the writer has made several ineffectual attempts to repeat this result with X-ray and light exposures, no difference being observable in whichever order the exposures were given. According to Bloch's experiments,[82] it would appear that in the case of abrasion followed by a light exposure apparent reversal is due to a reduction of light-sensitiveness caused by the abrasion. Bloch[78] also raised the question as to the production of a latent image by the action of hydrogen peroxide, quite the same in nature apparently as that produced by radiation effects, where it would certainly appear that a chemical explanation is required. The apparent alteration of the latent image after exposure, which Mees[83] attributes in some cases to questions of moisture content, may also have a bearing on the problem. Lorenz and Hiege[84] have examined in the ultramicroscope the effect on silver chloride and bromide of continued light action and get appearances which they attribute to the formation of colloidal silver (see also Lüppo-Cramer's explanation of continued printing by yellow light, mentioned previously).

The question of the measurement of plate speeds and other constants is still awaiting standardization, as to lights employed, methods of exposure, and measurement of density. Renwick[85] has an interesting communication in which he shows the bearing of Schwarzschild's law (for equal effects $i_1^q t_1 = i_2^q t_2$), on ordinary photographic practice and on the determination of plate speeds. For instance, assuming a value of $q = 1{\cdot}16$, a reduction of light intensity to $\frac{1}{60}$th requires an increase of exposure of 115 times instead of 60 times. Weber[86] has examined the value of the rotating sector as a means of

[81] *Koll. Zeit.*, 1916, **18**, 18–20; *Chem.-Zeit.*, 1916, **40**, Rep. 304.
[82] *Phot. J.*, 1915, 219–227.
[83] *Astro-Phys. J.*, 1914, **40**, 236; *Sci. Abs.*, 1915, 22.
[84] *Z. Anorg. Chem.*, 1915, 27–34; *J.* 1916, 708.
[85] *Phot. J.*, 1916, 11–13.
[86] *Ann. der Phys.*, 1914, 801–838; *Sci. Abs.*, 1915, 223.

obtaining the scale of known exposures, and has concluded that the method is quite satisfactory for ultra-violet rays and, apparently, also for light rays; in view of the considerable amount of evidence as to the failure of the method due to intermittency error the result is not very convincing.

The Hurter and Driffield system of examining plates as to speed and gradation has been applied to the study of photographic papers by Jones, Nutting, and Mees.[87] An ingenious instrument was devised for determining the reflection density of a deposit ($D_r = \log \frac{1}{R}$, where R is the fraction of light reflected), in which the density was illuminated at 45 degrees and viewed at 90 degrees so as to obviate the interference of specular reflection. They show a similarity between the characteristic curves of plates and papers, there being in each case periods of under-exposure, correct exposure, and over-exposure. Accepting the direct proportionality between mass of silver and transmission density, they suggest $D_r = \log \frac{1}{(1-C)\,T^2 R_p + C}$, where C is the surface reflection, T the transmission of the deposit and R_p the reflecting power of the paper; taking $C = 0{\cdot}01$ and $R_p = 0{\cdot}88$, the curve with masses of silver as abscissæ and values of D_r as ordinates is concave to the x-axis and reaches a maximum at about $D_r = 2$. It is doubtful, however, as pointed out by Renwick in discussing the paper, whether C can be regarded as constant. The authors discuss what they regard as the constants on which the quality of a photographic paper depends and give a number of tables and figures showing the ranges and particulars of various types of paper. The value of the whole paper, however, is seriously depreciated by the neglect to take account of the fact that a paper is not necessarily intended to reproduce a negative, but, through a negative as intermediate stage, to reproduce the original. If there is any departure in the negative from the gradation of the original, then, if possible, correction should be made in the positive. In a large amount of photographic work a considerable part of the negative may be on the under-exposure part of the curve; in most prints also the under-exposure period is used. The importance of this part of the curve was emphasised by Renwick[88] in 1913, and he drew attention to it again in the discussion[87] following the paper just mentioned. More work is necessary before the full effect of the whole characteristic curve on photographic practice is satisfactorily explained.

[87] *Phot. J.*, 1914, 342–358; 1915, 29–30; *J.*, 1915, 250–251.
[88] *Phot. J.*, 1913, 127–142.

Some interesting work on diffusing media has been published by Nutting and others[89] in America and by Bloch and Renwick[90] in this country. The former was part of a report on various optical problems presented to the Society of Illuminating Engineers, P G. Nutting being the chairman of the sub-committee dealing with this section, and is unfortunately not accompanied by many experimental data. The main conclusions were that the opacity of diffusing media is like the opacity of negatives and of non-diffusing media, proportional to thickness, and that the increase of reflection with thickness follows an exponential law. Their method of measuring opacity is indicated. Bloch and Renwick approached the subject from a somewhat different standpoint, wishing to determine the relationship between the opacity and the photographic qualities of a sensitive film. They were able to confirm Abney's statement that the effective density of a diffusing medium is not proportional to thickness. They also arrived at an empirical formula $D = a\ W^b$, where D is density, W weight per unit area or thickness, and a and b are constants depending on the substance and method of measurement; where $b = 1$, D is proportional to W. They found the measurement of opacity, however, a difficult matter, the results varying considerably with alterations of details of conditions, and although they were able to get $b = 1$ in the above equation for opal glass under certain conditions, they were unable definitely to confirm Nutting's generalization.

The question of the resolving power of photographic plates, previously discussed by Scheffer, Mees, Goldberg, and others, has been attacked again by Tugman.[91] He adopted a method suggested by Nutting, using a straight-edge in contact with the film to obtain a definite limit to the exposed part, and examined the spreading of the image on the unexposed part. The density gradient of this edge is dependent on the light distribution and on the photographic qualities of the plate and is taken as a measure of the resolving power. The edge is very narrow and some difficulty was experienced in measuring the change of density with distance. A Koch photo-micrometer was tried, but was not so satisfactory as a combination of a König-Martens polarization photometer with a microscope.

Comparisons of the values of various light sources for photographic purposes have been made by E. J. Wall,[92] Jones, Hodgson and Huse,[93]

[89] *Trans. Amer. Ill. Eng. Soc.*, vol. x, No. 5.

[90] *Phot. J.*, 1916, 49–67; *J.*, 1916, 385–386.

[91] *Phot. J.*, 1915, 292–302; *J.*, 1916, 143; see also Channon, *Phot. J.*, 1916, 74; *J.*, 1916, 386.

[92] *Phot. J. Amer.*, 1916, 171–173.

[93] *B.J. Colour Supplement*, 1915, 43, 44, 47, 48, and 1916, 8.

and Lux.[94] The last two papers take account of almost all the light sources used in photography, and the former of these also discusses visual efficiencies.

Amongst other interesting items recently published are some on the light-sensitiveness of various substances. Wood-pulp paper and pure photographic raw paper[95] are both light sensitive, and the images can be developed to a deep brown with pyro-soda. Dr. Molisch[96] has obtained a photograph on a leaf showing the formation of starch by light action, while Prof. Blackman[97] has succeeded in taking photographs by use of the tiny natural lenses on the upper surface of plant leaves. Goedrich[98] has found that the vulcanizing of thin rubber sheets can be effected as easily by the ultra-violet light of a mercury vapour lamp as by heat. Goedrich[99] and Rosinger[100] have both examined the light-sensitiveness of asphalts and find the effect of light action to be an oxidation process, the presence of oxygen being necessary and the oxidation proceeding slowly in the dark ; the effect is partly one of adsorption when sensitizers such as safrol and eugenol are present. Eder[101] finds pure mercuric oxalate to be light-sensitive, chiefly to the ultra-violet, still more so if traces of iron are present. Winther and Oxholt-Howe[102] have examined the light-sensitiveness of ferric salts of various organic acids in monochromatic light of various wave-lengths.

Sahni[103] has examined the action of α-, β-, and γ-rays on photographic plates, using a radium salt on the point of a needle as the active body, and taking precautions to separate the rays to be tested. Nutting[104] has made experiments on the visibility of faintly illuminated objects, and concludes that the eye is distinctly more sensitive than a photographic plate. Michaud and Tristan[105] describe a method of sensitizing plates for infra-red photography, using Alizarin Blue S and

[94] *Deuts. Beleucht. Ges.*, Mar. 20, 1915; *Chem.-Zeit.*, 1915, **39**, 539-540; *J.*, 1915, 1226.

[95] Liesegang, *Phot. Korr.*, 1915, 173; *Phot. J. Amer.*, 1916, 35.

[96] *Phot. J. Amer.*, 1915, 158.

[97] *B.J.*, 1915, 356.

[98] *Phot. Korr.*, 1915, 202; *Phot. J. Amer.*, 1916, 35.

[99] *Monatsh. Chem.*, 1915, 535–548; *J. Chem. Soc.*, 1915, i, 978–979; *J.*, 1915, 1273; *Chem.-Zeit.*, 1915, 832; *J.*, 1916, 73.

[100] *Koll. Zeit.*, 1914, 177–179; *J.*, 1915, 687.

[101] *Z. wiss. Phot.*, 1914, 172–176; *J. Chem. Soc.*, 1915, ii, 199–200; *J.*, 1915, 687.

[102] *Z. wiss. Phot.*, 1914, 196–212; *J.*, 1915, 687.

[103] *Phil. Mag.*, 1915, 836–841; *J.*, 1915, 736.

[104] *Nature*, 1914, 480; *Sci. Abs.*, 1915, 19.

[105] *Scien. Amer.*, 1914, 521 and 531; *B.J.*, 1915, 56.

silver nitrate in ammoniacal solution. Bull and Jolley[106] find it a general rule with coloured substances that a high transmission of one part of the spectrum is accompanied by complete absorption of another part only when the former region is of longer wave-length than the latter, so that a bright blue one-sided absorption dye is not to be expected. Peskov[107] has examined the absorption of dry chlorine and bromine vapour, especially in the ultra-violet, and finds that filters may be made, by varying the concentrations, for any part of the ultra-violet, and with quite narrow bands. Padoa and Minganti[108] have examined the variation of the temperature coefficient of the reaction between mercuric chloride and ammonium oxalate according to the wave-length of the light employed. Hartridge[109] finds it possible to produce, by a suitable selection of dyes, a light-filter which is almost white in appearance but still safe for some dark-room purposes, and has patented the process. As, however, he has found it necessary to cut out more green to get a light suitable for use with fast plates, his process does not finally differ very much from that of Ilford Limited, and possibly other firms, who take advantage of the lesser sensitiveness of most photographic plates and development papers to yellow-green than to orange-red, to produce safe lights safer and pleasanter to work by than the usual ruby.

A useful list of formulæ for single band light-filters for all parts of the spectrum, and of varying widths, is given by Hnatek.[110] Valenta[111] has described a method for detecting the presence of silver chloride in photographic papers depending on the preferential formation of the ferrocyanide.

[106] *Phot. J.*, 1915, 134–140.

[107] *J. Russ. Phys. Chem. Soc.*, 1915, 918–942; *J. Chem. Soc.*, 1915, ii, 716–717; *J.*, 1915, 1272.

[108] *Atti R. Accad. Lincei*, 1915, [v], **24**, ii, 97–101; *J. Chem. Soc.*, 1915, ii, 719–720; *J.*, 1915, 1273.

[109] Eng. Pat. 17789, 1914.

[110] *Zeit. wiss. Phot.*, 1915, 133; *Phot. J. Amer.*, 1915, 591.

[111] *Chem.-Zeit.*, 1916, 398; *J.*, 1916, 655.

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